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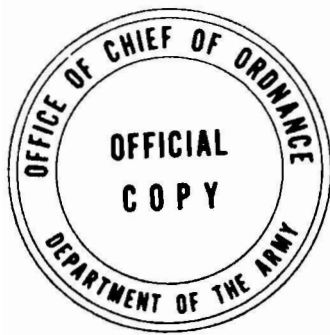
PROPULSION AND PROPELLANTS

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PROPULSION AND PROPELLANTS

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Preface

This Handbook has been prepared as one of a series on Ballistic Missiles. It presents information on the fundamental operating principles of propulsion systems as found in ballistic missiles, with discusions of propellants which have been found practicable or which have theoretically attractive possibilities. Criteria are presented whereby the performance of propulsion systems can be judged.

The handbook was prepared for the Office of Ordnance Research, Ordnance Corps, U. S. Army. The text and illustrations were prepared by Vitro Laboratories under contract with Duke University, with the technical assistance of Army Ballistic Missile Agency and the Special Projects Branch of Navy Bureau of Ordnance.

Comments on, and requests for copies of, this Handbook should be addressed to Commanding Officer, Office of Ordnance Research, U. S. Army, Box CM, Duke Station, Durham, N. C.

PROPULSION AND PROPELLANTS

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Chapter 1

INTRODUCTION *

1-1. DEFINITIONS AND SCOPE

All known methods of propelling a body through the earth's atmosphere are based on Newton's principle, for every action there is an equal and opposite reaction. In a dynamic system a mass is accelerated in a given direction by producing a reaction force acting in the opposite direction. Hence, a jet propulsion engine derives its thrust from the fluid accelerated through the engine to emerge as a high speed jet of propulsive power at the tail of the engine. The high speed fluid jet is termed the propulsive jet, and the reaction force that propels the vehicle is termed thrust. The thrust acting in the direction of motion of the propelled vehicle has a direction that is always opposite to that of the high speed fluid jet.

For propelling either an aircraft or a missile through the earth's atmosphere the most suitable fluid for forming the propulsive jet is a hot gas. Jet propulsion engines for propelling such vehicles are basically devices for producing propulsive jets formed of hot gases and may be grouped into two broad classes, depending upon the methods employed for producing the hot, gaseous, propulsive jets:

1. thermal jet engines, which consume atmospheric air in creating the propulsive jet
2. rocket engines,[1] which create the propulsive jet by reacting suitable chemicals and do not consume any atmospheric air.

The principal types of thermal jet engines are the turbojet engine, the ramjet engine, and the pulsejet engine. Currently, thermal jet engines are not employed either for launching or propelling

ballistic missiles, and therefore no discussion of thermal jet engines will be presented in this volume. For information on those engines the reader is referred to references 1 and 2 at the end of this chapter.

The propulsion engines employed for propelling ballistic missiles are chemical rocket engines. Chemicals consumed in creating the propulsive jet are termed propellants. There are two main classes of rocket engines:[2]

1. liquid propellant rocket engines, which burn chemicals that are in a liquid state prior to combustion
2. solid propellant rocket motors, which burn chemicals which are in a solid state prior to combustion.

Since World War II all military services in the United States Department of Defense have been actively engaged in applying rocket jet propulsion to weapon systems. All have developed, or are developing, rocket jet propelled ballistic missiles.

This volume covers the fundamental principles governing the operation and performance of chemical rocket engines for ballistic missiles. Introductory Chapter 1 presents a review of basic thermodynamic relationships with definitions of principal terms. This is followed by a description of the essential features of rocket engines in Chapter 2 and a discussion of rocket engine performance criteria in Chapter 3. Chapter 4 deals with the application of thermodynamic relations to rocket engines, and in Chapters 5 and 6 the properties and characteristics of liquid propellants and solid propellants are examined.

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* This volume was written by M. J. Zucrow, Director of Jet Propulsion Laboratory, Purdue University, and edited by C. D. Fitz, Vitro Laboratories.

[1] In this handbook the phrase *rocket engine* is occasionally employed as the generic term covering all non-air-breathing reaction propulsion devices. According to a recent change in Cataloging Handbook H6-1, a publi-

cation of the Assistant Secretary of Defense (Supply and Logistics), liquid fuel units are designated as *rocket engines* and solid fuel units as *rocket motors*.

[2] A propulsive jet can be formed in other ways than by direct chemical reaction; for example, by heating a working substance in a nuclear reactor. Discussions in this handbook are limited to chemical rockets.

1-2. BASIC UNITS OF MEASUREMENT

The basic units of measurement used in this handbook, unless specifically stated to be otherwise, are listed below (1).[1]

Dimension	Basic Unit
mass	1 slug
force	1 pound (lb)
length	1 foot (ft)
time	1 second (sec)

Table 1-1 indicates the abbreviations used in measurement units.

Table 1-2 presents a list of conversion factors.

Table 1-3 gives the principal notations used in this volume.

TABLE 1-1. PRINCIPAL ABBREVIATIONS OF MEASUREMENT UNITS

Abbreviation	Quantity
Btu	British thermal unit
°C	degrees Centigrade
cc	cubic centimeters
°F	degrees Fahrenheit
g	gram
°K	degrees Kelvin
kg	kilograms
lb	pounds
psi	pounds per square inch
psia	pounds per square inch absolute
pcf	pounds per cubic foot
°R	degrees Rankine

1-3. REVIEW OF BASIC THERMODYNAMIC RELATIONSHIPS

The temperature of the combustion gas produced in the combustion chamber of a rocket motor is well above the critical temperatures for its individual gaseous species. Moreover, the combustion pressures are generally moderate compared to the critical pressures for the constituent gases. It is customary, therefore, to assume that the combustion gas behaves in accordance with the laws for perfect gases.[2] For convenience of reference, the basic relationships for perfect gases will be reviewed.

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[1] Numbers in parentheses in the text indicate references listed at the end of the chapter.

[2] Modifications must be made in the case where the combustion gas contains solid particles or vaporized solids; the latter may undergo a phase change during

1-3.1. Equation of State for a Perfect Gas.

Let p denote the absolute static pressure, t the absolute static temperature, $\overline{m}$ the molecular weight of the gas, and v its specific volume. Then

$$pv = \frac{R_u}{\overline{m}} \ t = Rt \qquad (1-1)$$

where R_u = the universal gas constant, and $R = 1545/\overline{m}$ = the gas constant for the specific gas.[3]

If $v_{\overline{m}} = \overline{m}v$ = the volume of one mole of a perfect gas, then

$$p \ v_{\overline{m}} = R_u \ t \qquad (1-2)$$

1-3.2. Dalton's Law.

If p_m denotes the total static pressure exerted by a mixture of gases having the initial partial pressures $p_1, p_2, \cdots p_n$, then

$$p_m = p_1 + p_2 + \cdots p_n = \sum_{i=1}^{n} p_i \qquad (1-3)$$

where p_i = partial pressure of i-th species.

The molecular weight of the mixture of gases $\overline{m}_m$, is given by

$$\overline{m}_m = \frac{\sum_{i=1}^{n} n_i \ \overline{m}_i}{\sum_{i=1}^{n} n_i} \qquad (1-4)$$

where n_i is the number of moles of i-th species, and $\overline{m}_i$ is its molecular weight.

Let
$$n_m = \sum_{i=1}^{n} n_i$$

Then
$$n_i = p_i \frac{n_m}{p_m} = p_i \frac{v_m}{R_u t_m} \qquad (1-5)$$

where v_m and t_m denote respectively the volume and absolute temperature of the gas mixture.

Equation (1-5) shows that in a mixture of perfect gases the number of moles of the i-th species is proportional to its partial pressure p_i.

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the expansion process in the nozzle. (Reference 3, 4)

[3] $R_u = 1.9864$ Btu/°R lb-mol = 1.9864 cal/°K g-mol = 1545 ft-lb/°R lb-mole (Principal Notations are presented in Table 1-3).

TABLE 1-2. CONVERSION FACTORS

Given	Multiply by	To obtain
FORCE		**FORCE**
dynes	1.020×10^{-6}	kilograms
kilograms	2.205	pounds
pounds	32.174	poundals
	4.448×10^{5}	dynes
PRESSURE		**PRESSURE**
atmospheres	14.70	pounds per sq in
	1.0132×10^{6}	dynes per sq cm
	29.92	inches of mercury
bars	10^{6}	dynes per sq cm
dynes per sq cm	2.953×10^{-5}	inches of mercury
	7.501×10^{-4}	millimeters of mercury
pounds per sq in	2.036	inches of mercury
	5.1715×10	millimeters of mercury
MASS		**MASS**
grams	2.205×10^{-3}	pounds
pounds	4.535×10^{3}	grams
slugs	32.174	pounds
	14.594×10^{3}	grams
LENGTH		**LENGTH**
centimeters	0.03281	feet
feet	30.48	centimeters
inches	2.540	centimeters
microns	10^{-4}	centimeters
angstroms	10^{-8}	centimeters
VOLUME		**VOLUME**
cubic feet	2.832×10^{4}	cubic centimeters
	7.481	gallons
	28.32	liters
cubic inches	16.39	cubic centimeters
gallons	3.785	liters
liters	0.03532	cubic feet
DENSITY		**DENSITY**
grams per cm³	0.03613	pounds per cubic inch
	62.43	pounds per cubic foot
pounds per in³	27.68	grams per cubic centimeter
ENERGY		**ENERGY**
British thermal units	251.8	calories
	2.931×10^{-4}	kilowatt-hours
calories	3.968×10^{-3}	British thermal units
POWER		**POWER**
Btu per hour	3.930×10^{-4}	horsepower
	2.931×10^{-4}	kilowatts
horsepower	2.544×10^{3}	Btu per hour
TEMPERATURE		**TEMPERATURE**
degrees Kelvin	1.0	degrees Centigrade + 273.2
	1.8	degrees Rankine
degrees Centigrade	1.8	degrees Fahrenheit − 32
degrees Rankine	1.0	degrees Fahrenheit + 459.7

TABLE 1-3. PRINCIPAL NOTATIONS

a_c	acoustic velocity for combustion gases			32.1740 ft/sec²)
a_i	moles of i-th species of reactants		h	specific enthalpy
$(a_i)_o$	initial moles of reactants		h_c	static specific enthalpy entering exhaust nozzle
A	cross-sectional area			
A_c	cross-sectional area of case surrounding grain		h'_e	specific enthalpy of gases at exit of nozzle for isentropic enthalpy change
A_e	cross-sectional area of nozzle exit section		$\Delta h'_i$	enthalpy change for isentropic expansion
A_F	frontal area			
A_G	cross-sectional area of the propellant grain		H_c	stagnation specific enthalpy of gases entering exhaust nozzle
A_i	denotation for reactants		H_f^o	enthalpy of formation at reference temperature
$(A_i)^{a_i}$	partial pressure of species A_i			
A_m	maximum cross-sectional area of missile		ΔH_r	total enthalpy of reaction
A_p	port area		$\Sigma(\Delta H_f)_p$	sum of enthalpies of formation for the individual products
A_t	nozzle throat area			
b_j	molar concentration of j-th species of products		$\Sigma(\Delta H_f)_R$	sum of enthalpies of formation for the individual reactants
Btu	British thermal unit		I	total impulse
B_j	denotation for reaction product		I_d	density impulse
$(B_j)b_j$	partial pressure of species B_j		I'_d	theoretical density impulse
$(B_j)_{t_c}$	moles of products at the temperature t_c		I_s	specific impulse
c^*	characteristic velocity for rocket propellant		I'_s	theoretical specific impulse
			J	mechanical equivalent of heat (778 ft-lb/Btu)
c_p	specific heat at constant pressure			
c_v	specific heat at constant volume		k	specific heat ratio $\left(\dfrac{c_p}{c_v}\right)$
C_d	discharge coefficient for a nozzle or orifice		K_n	$\dfrac{S_p}{A_t}$, propellant area ratio
C_F	thrust coefficient			
C'_F	theoretical value of C_F		K_p	equilibrium constant
C_m	mass flow coefficient		L^*	characteristic length of rocket motor
C_p	molar specific heat at constant pressure		ln	log to base e
C_v	molar specific heat at constant volume		$\dot{m}$	mass rate of propellant consumption
$\bar{C}_v$	mean value of C_v		m	mass
C_w	weight flow coefficient		$\bar{m}$	molecular weight
d_i	inner diameter of grain		m_b	instantaneous mass of missile
d_o	outer diameter of grain		$\bar{m}_j$	molecular weight of j-th component
D	drag		$\bar{m}_m$	molecular weight of mixture of gases
F	thrust		M_c	Mach number for gases at entrance to exhaust nozzle
$\Delta \mathcal{J}^o$	standard free energy change			
$\mathcal{J}_{A_i}$	free energies of species A_i		$\Delta \underset{\sim}{M}$	change in momentum of body or fluid
$\mathcal{J}_{A_i}^o$	standard free energy of species A_i		M_o	initial mass of vehicle
$\mathcal{J}_{B_j}$	free energies of species B_j		M_p	effective mass of propellants
$\mathcal{J}_{B_i}^o$	standard free energies of B_j		n	burning rate exponent or pressure index
g	gravitational acceleration, general		n_i	moles of i-th species of gas
g_o	gravitational acceleration (standard		n_j	mole fraction of j-th component

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TABLE 1-3. (Continued)

N	number of moles of gas mixture	W_{EO}	take-off weight of rocket propulsion system
p	absolute static pressure	$\dot{W}_f$	fuel flow rate
p_c	gas pressure at entrance to exhaust nozzle	W_G	weight of guidance equipment and housing
p_e	gas pressure at exit of nozzle	W_I	weight of empty missile
p_i	static pressure acting on interior surface of the rocket motor	W_M	weight of missile inert metal parts
p_m	static pressure exerted by mixture of gases	$\dot{W}_o$	oxidizer flow rate
p_o	standard sea level static pressure	W_o	weight of loaded missile
P_c	stagnation value of gas pressure	W_p	total weight of propellants
Q	quantity of heat	W_S	structural weight of missile
Q_{avail}	available heat	$\dot{W}_s$	specific propellant consumption
Q_f	heat of formation	W_T	weight of missile propellant tanks
Q_v	heat of vaporization	W_U	weight of payload

$r = \dfrac{\dot{W}_o}{\dot{W}_f}$, fuel mixture ratio

$Z_t = 1 - \theta_t$, the expansion factor

r	linear burning rate for a solid propellant		
r_o	linear burning rate for $V_g = 0$		
R	gas constant		
R_u	universal gas constant		
S_i	interior surface of rocket motor		
S_o	exterior surface of rocket motor		
S_p	area of burning surface of a solid propellant grain		
s	entropy		
t	absolute static temperature		
t_c	combustion temperature		
t_e	gas temperature at exit of nozzle		
t'_e	isentropic exit temperature		
t_m	absolute temperature of gas mixture		
u	specific internal energy		
v	specific volume		
v_m	volume of gas mixture		
V	missile velocity		
V'	isentropic velocity		
V_{bi}	ideal burnout velocity		
V_c	velocity of combustion gases at entrance section of exhaust nozzle		
V_e	velocity of gases at exit section of nozzle		
V'_e	isentropic exit velocity		
V_{ex}	x component of velocity for exhaust jet		
V_g	velocity of combustion gas parallel to burning surface (for end burning grain $V_g = 0$)		
V_j	effective exhaust velocity		
V_p	volume of propellant grain		
w	web thickness of grain		
$\dot{W}$	weight rate of propellant consumption		
W_C	weight of missile control apparatus		
W_E	dry weight of complete rocket engine		

Greek letters

α	semi-divergence angle for exhaust nozzle
γ	specific weight of an incompressible fluid
γ_p	specific weight of propellant
σ_p	propellant weight loading density or engine weight efficiency

$\epsilon = \dfrac{A_e}{A_t}$, area ratio

$\epsilon_p = \dfrac{A_G}{A_C}$, propellant loading ratio

$\epsilon_{pt} = \dfrac{A_P}{A_t}$, port-to-throat ratio

$\zeta =$ velocity coefficient

$\xi = \dfrac{M_p}{M_O}$, propellant mass ratio

$\theta_t = \left(\dfrac{p_2}{p_1}\right)^{(k-1)/k}$, expansion ratio parameter

λ divergence coefficient for nozzle

$\Lambda = \dfrac{M_O}{M_O - M_p} = \dfrac{M_O}{m_b}$, vehicle mass ratio

μ	viscosity
π_{ro}	temperature sensitivity coefficient
π_f	thrust temperature coefficient
π_{pc}	combustion pressure temperature coefficient
ρ	density
$\bar{\rho}_p$	average density of propellant system (fuel + oxidizer)
τ	time
τ_b	burning time
Ψ	flow factor
Ω	a function of k

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1-3.3. Internal Energy. Internal energy, denoted by u, is a thermodynamic property whose value is independent of the process employed for bringing the system to a given state. For a perfect gas, u is a function only of the gas temperature t, and

$$du = c_v \, dt \qquad (1-6)$$

where c_v is the specific heat at constant volume for the gas, and is in general, a function of t.

The molar specific heat at constant volume is denoted by C_v and is given by

$$C_v = \overline{m} \, c_v \qquad (1-7)$$

For monatomic gases the molar specific heat is a constant and has the value $C_v = 2.981$ cal per g-mol° K.

1-3.4. Relationship Between Specific Heats. For a gas, if c_p denotes the specific heat at constant pressure (Btu/lb R), then

$$\overline{m}(c_p - c_v) = C_p - C_v = R_u \qquad (1-8)$$

The specific heat ratio, denoted by k, is defined by

$$k = \frac{C_p}{C_v} = \frac{c_p}{c_v} \qquad (1-9)$$

From equations (1-7) and (1-8) it follows that

$$C_p = \overline{m} c_p = R_u \frac{k}{k-1} \qquad (1-10)$$

and

$$C_v = \overline{m} c_v = R_u \left(\frac{1}{k-1}\right) \qquad (1-11)$$

Table 1 presents $C_p = \overline{m} c_p$ for several gases as a function of temperature.[1]

Let $\bar{C}_v$ denote the mean value of C_v for the temperature range t_o to t. Then

$$\bar{C}_v = \frac{1}{t - t_o} \int_{t_o}^{t} C_v \, dt \qquad (1-12)$$

1-3.5. Enthalpy of a Perfect Gas. The thermodynamic property called enthalpy (also known as total heat) is defined by

$$h = u + \frac{pv}{J} \qquad (1-13)$$

where h is the enthalpy per unit weight or the specific enthalpy, and J is the mechanical equivalent of heat. For a perfect gas

$$dh = c_p \, dt \qquad (1-14)$$

Since h for a gas is a function of temperature its values measured above some base temperature t_o (for which h_o is usually given the value zero) can be tabulated by using the values of c_p for zero pressure. Then $h = c_p t$. Table 2 presents the enthalpies of C-H-N-O compounds measured above $t_o = 298.16°$K.

1-3.6. Isentropic Change of State. For a reversible adiabatic process there is no transfer of heat ($\Delta Q = 0$) and the entropy of the system remains constant ($ds = 0$). Such a process is termed an isentropic process. If a perfect gas changes its state by an isentropic process, then

$$p_1 v_1^k = p_2 v_2^k = \text{constant} \qquad (1-15)$$

Also

$$\frac{t_2'}{t_1} = \left(\frac{p_2}{p_1}\right)^{(k-1)/k} = \left(\frac{p_2}{p_1}\right)^{R_u/C_p} = \left(\frac{p_2}{p_1}\right)^{R/Jc_p} \qquad (1-16)$$

The superscript prime (') attached to t_2 in equation (1-16) above denotes that state number 2 was reached by employing an isentropic process.

Consider an isentropic expansion ($p_2 < p_1$) from state number 1, where the specific enthalpy of the gas is h_1, to state number 2 where it is h_2'. If $\Delta h_t'$ denotes the isentropic enthalpy change, then

$$\Delta h_t' = h_1 - h_2' = \int_{1}^{2'} c_p \, dt \qquad (1-17)$$

If $\bar{c}_p$ denotes the mean value of c_p, then

$$\Delta h_t' = \bar{c}_p t_1 (1 - \theta_t) = \bar{c}_p t_1 Z_t \qquad (1-18)$$

where the expansion ratio parameter θ_t is given by

$$\theta_t = \left(\frac{p_2}{p_1}\right)^{(k-1)/k} \quad (\text{for } p_2 < p_1) \qquad (1-19)$$

and

$$Z_t = 1 - \theta_t = \text{the expansion factor} \qquad (1-20)$$

In the case of an expansion in the nozzle of a rocket motor $p_1 = p_c = $ the pressure at the inlet

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[1] Numbered tables will be found in the Appendix.

section to the exhaust nozzle (the combustion pressure), and $p_2 = p_e =$ the pressure in the exit section of the exhaust nozzle, called the exit pressure.

Appendix Table 3 presents values of the expansion ratio parameter θ_t as a function of p_e/p_c for different values of k.

1-3.7. Isentropic Velocity. If a perfect gas is expanded from state 1 to state 2 the resulting transformation of enthalpy into kinetic energy is given by

$$\frac{V^2}{2gJ} = h_1 - h_2 \qquad (1\text{-}21)$$

where h_1 and h_2 are the initial and final values of the specific enthalpy of the gas.

In the special case where the expansion process is isentropic, the final state is 2' and the corresponding values of specific enthalpy and temperature are h'_2 and t'_2 respectively. The velocity attained by the expanded gas is V', the isentropic velocity. Thus

$$V' = 2gJ(h_1 - h'_2) = 2gJ \, \bar{c}_p \, t_1 \, Z_t \qquad (1\text{-}22)$$

Values of $\sqrt{Z_t}$ as a function of p_c/p_e for different values of k are presented in Table 4.

Values of several functions of k are presented in Table 5.

1-3.8. The Free Energy Function. (5) The Gibbs free energy function, for brevity called free energy, is denoted by J and defined by

$$J = h - ts = u + pv - ts \qquad (1\text{-}23)$$

Since h, u, t, and s are thermodynamic properties the free energy J is likewise a thermodynamic property.

For an isothermal change of a perfect gas the corresponding free energy change is

$$(J - J^\circ)_t = R_u t \ln p \qquad (1\text{-}24)$$

where J° denotes the standard free energy at the absolute temperature t and 1 atm pressure.

The free energy J finds its principal use in establishing the criteria for predicting equilibrium of chemical and physical processes. For a system in equilibrium, J has its minimum value. Moreover, for a process to take place spontaneously under the conditions $\Delta t = \Delta p = 0$ the corresponding free energy change, denoted by ΔJ_{tp}, must be negative. For a system which is in equilibrium

$$\Delta J_{tp} = 0 \qquad (\Delta p = \Delta t = 0) \qquad (1\text{-}25)$$

The equilibrium chemical reactions for rocket propellants are of particular interest because the equilibrium composition of the gas mixture at the entrance to the exhaust nozzle, the combustion temperature and pressure, and the characteristics of the exhaust nozzle, all determine the jet velocity, and hence the specific impulse obtainable from the propellants.

When the reactants in a chemical equation are elements, such as oxygen and hydrogen, and they react to form a single chemical compound, such as water, the free energy change ΔJ_{tp} for the reaction is termed the free energy of formation.[1] When the reaction takes place under standard conditions (usually 1 atm and either 298.16°K or 300°K) it is termed the standard free energy of formation and is denoted by J_f°.

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[1] As is the case in calculating the enthalpy (or heat) of formation for a chemical compound, the free energy of formation for any chemical element is zero.

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Chapter 2

ESSENTIAL FEATURES OF ROCKET ENGINES

2-1. GENERAL OPERATING PRINCIPLES (1, 2)

Figure 2-1 illustrates schematically the main components of a fin-stabilized solid propellant rocket motor. It is the element which produces the propulsive thrust. A rocket motor comprises a solid propellant grain or charge, enclosed in a metal housing, a De Laval type of exhaust nozzle, an igniter for igniting the propellant grain, and electrical leads for supplying the electrical energy for firing the igniter. (3)

Consider a solid propellant rocket motor. As the propellant grain burns it produces tremendous quantities of hot gas. If the propellant burns at a constant rate in a closed chamber such as illustrated in Figure 2-2a, the gas pressures inside the chamber are always balanced in all directions, and because there is no unbalanced pressure force no thrust is developed. Let a hole now be opened in one end of the chamber, as illustrated in Figure 2-2b, and assume that the propellant burns at a constant rate. The combustion pressure inside the chamber will remain constant (a short time after the grain is ignited) at a value governed by the area of the hole and the rate at which the propellant burns. At the hole there is an escape of gas and the latter has no surface against which it can push. Hence, there is an unbalanced pressure force, denoted by F, acting to the left. In an actual rocket motor the hole in Figure 2-2b is replaced by a De Laval nozzle, as illustrated in Figure 2-2c.

The conditions in the case of a liquid propellant rocket engine are similar. But in that type of rocket engine the hot gases are produced by burning one or more liquid propellants. Figure 2-3 illustrates schematically the main components of a liquid propellant rocket engine.

Regardless of whether solid or liquid propellants are burned in a rocket engine the main objective is to produce a propulsive jet having the largest possible ejection velocity, called the jet velocity.

Since the pressure of the gas at the entrance to the exhaust nozzle, denoted by p_c, will range from $p_c = 150$ to $p_c = 3000$ psia and the maximum pressure of the surroundings into which they discharge is $p_o = 14.7$ psia, the standard sea level static pressure, the pressure ratio for the exhaust nozzle p_c/p_o is always much larger than the critical pressure ratio for the combustion gas (see Chapter 4, reference 1). Consequently, the mean velocity of the gas crossing the throat section of the nozzle may be assumed to be equal to the local speed of sound. (7)

2-2. SALIENT FEATURES OF ROCKET JET PROPULSION

The functioning of a rocket engine differs fundamentally from that of an air-consuming engine by virtue of the following two characteristics:

1. a rocket engine consumes no atmospheric air, and
2. the thrust it develops, in lb per lb per sec of propellant consumption, $(F/\dot{W})$, depends only upon the jet velocity. In the case of an air-consuming engine thrust depends upon the difference between the jet velocity and that of the air entering the engine. (1, 2)

As a consequence of these characteristics rocket jet propulsion, compared with other known methods of propulsion, has the following advantages (4):

1. thrust is essentially independent of the flight speed
2. the thrust is substantially independent of the surrounding environment
3. thrust per unit of frontal area (F/A_F) is the largest for all known types of engines
4. thrust per unit of engine weight (F/W_E) is the largest of any known type of engine
5. there is no altitude ceiling
6. useful work increases directly with flight speed.

9
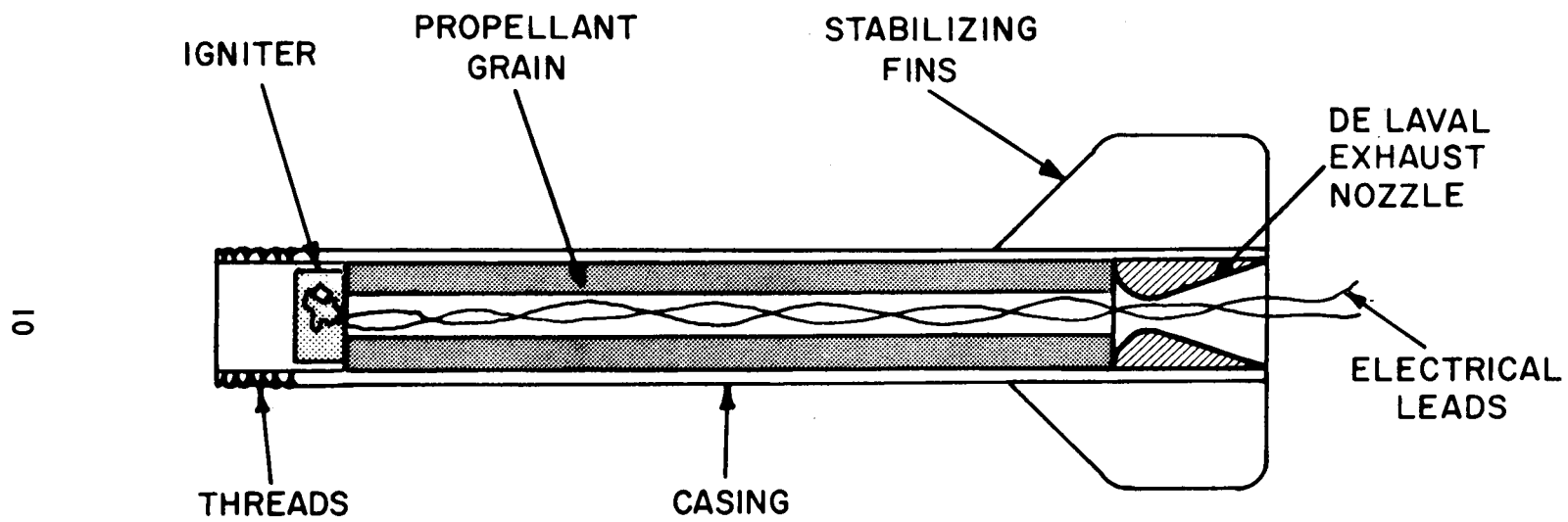
Figure 2-1. Fin-Stabilized Rocket Motor

ALL PRESSURES ARE BALANCED

(a)

RADIAL PRESSURES ARE BALANCED

F

(b)

THIS PRESSURE IS NOT
BALANCED, SO A THRUST
IS DEVELOPED

(c)

PROPELLANT GRAIN   CASE   DE LAVAL
EXHAUST
NOZZLE
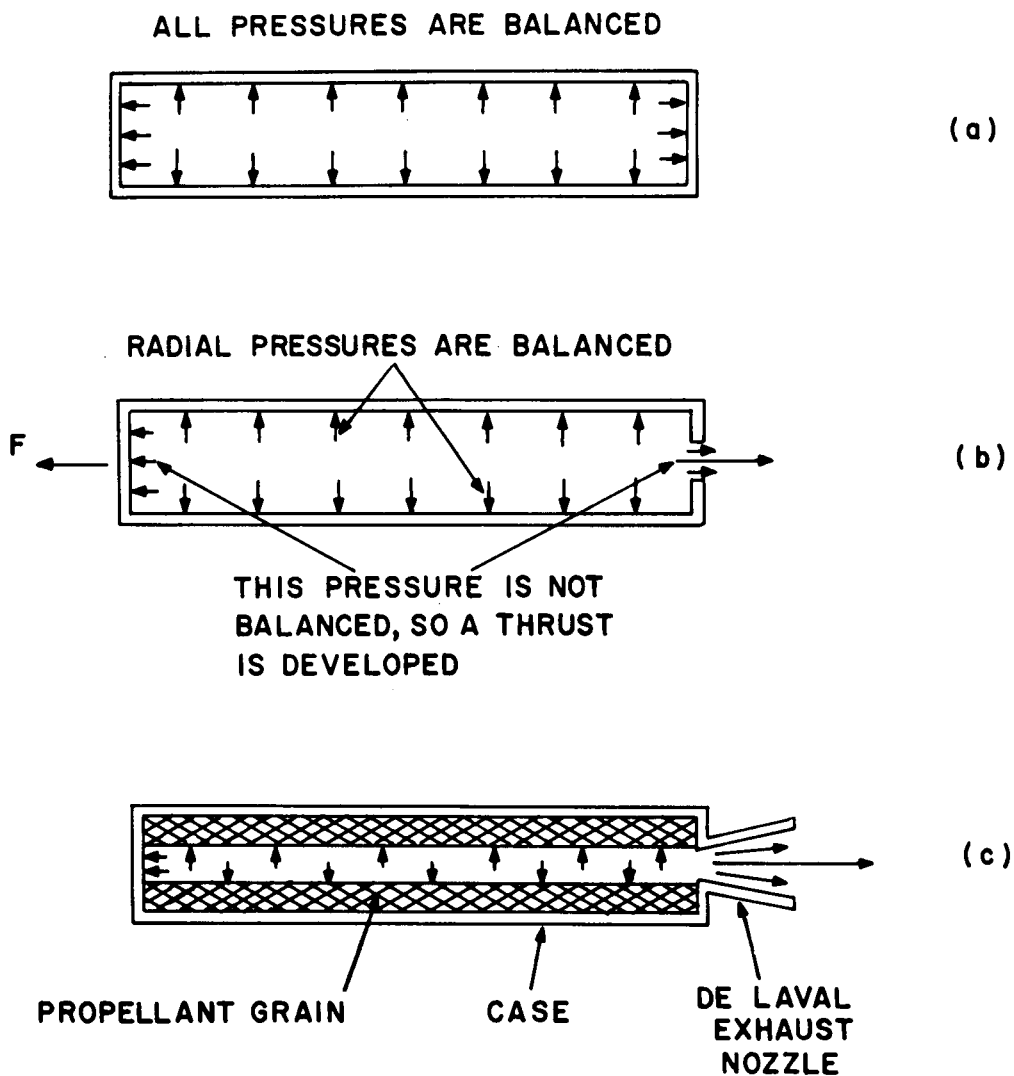
Figure 2-2. Development of Thrust in a Rocket Motor

$F = THRUST$

COMBUSTION CHAMBER   THROAT SECTION

p_o A_e

p_o

LIQUID
PROPELLANTS

V_c t_c

p_c p_e V_j p_o

p_c

S_i

INJECTOR

α

S_o p_o

DIVERGENCE
SEMIANGLE

x

Figure 2-3. *Principal Components of an Uncooled Liquid Propellant Rocket Engine*

Early workers in rocket jet propulsion recognized that these characteristics gave rocket jet propulsion the capabilities for attaining extremely high flight speeds and altitudes, and also the potentialities for making space flight a possibility.

Because oxygen for burning the fuel is not taken from the surrounding atmosphere, the rate at which a rocket engine consumes its propellants (fuel plus oxidizer) is several times that at which an air-consuming engine consumes fuel.

The most important parameters governing the speed of flight are F/A_F, the thrust per unit of frontal area[1], and F/W_E, the thrust per unit of engine weight. As mentioned earlier, judged by those parameters the rocket engine is unsurpassed. The range of flight for winged aircraft depends primarily on the thrust specific fuel consumption (TSFC) of the propulsion engine, measured in pounds of fuel per hour per pound of thrust.

To obtain a long range for a rocket propelled vehicle, such as a guided missile, a method must be utilized which takes advantage of its large values of F/A_F and F/W_E, but minimizes the adverse effects of its large TSFC. To achieve a long range, the large thrust of the rocket engine is utilized for propelling the vehicle to a very high altitude (several tens of miles), and for imparting to it a very large velocity (several thousands of feet per second), at the end of the operating period for the rocket engine, termed the powered flight. The velocity at the end of the powered flight is called either the cut-off velocity, burnout velocity, or burned velocity. The kinetic energy of the vehicle after it reaches the cut-off velocity is then used for coasting along a ballistic trajectory. Methods for computing the characteristics of ballistic trajectories are presented in another volume of this series.

2-3. CLASSIFICATION OF ROCKET ENGINES

Liquid propellant[2] rocket engines can be segregated into liquid monopropellant engines, and liquid bipropellant engines.

A solid propellant[3] rocket motor produces its

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[1] This parameter is important only for flight in the earth's atmosphere.
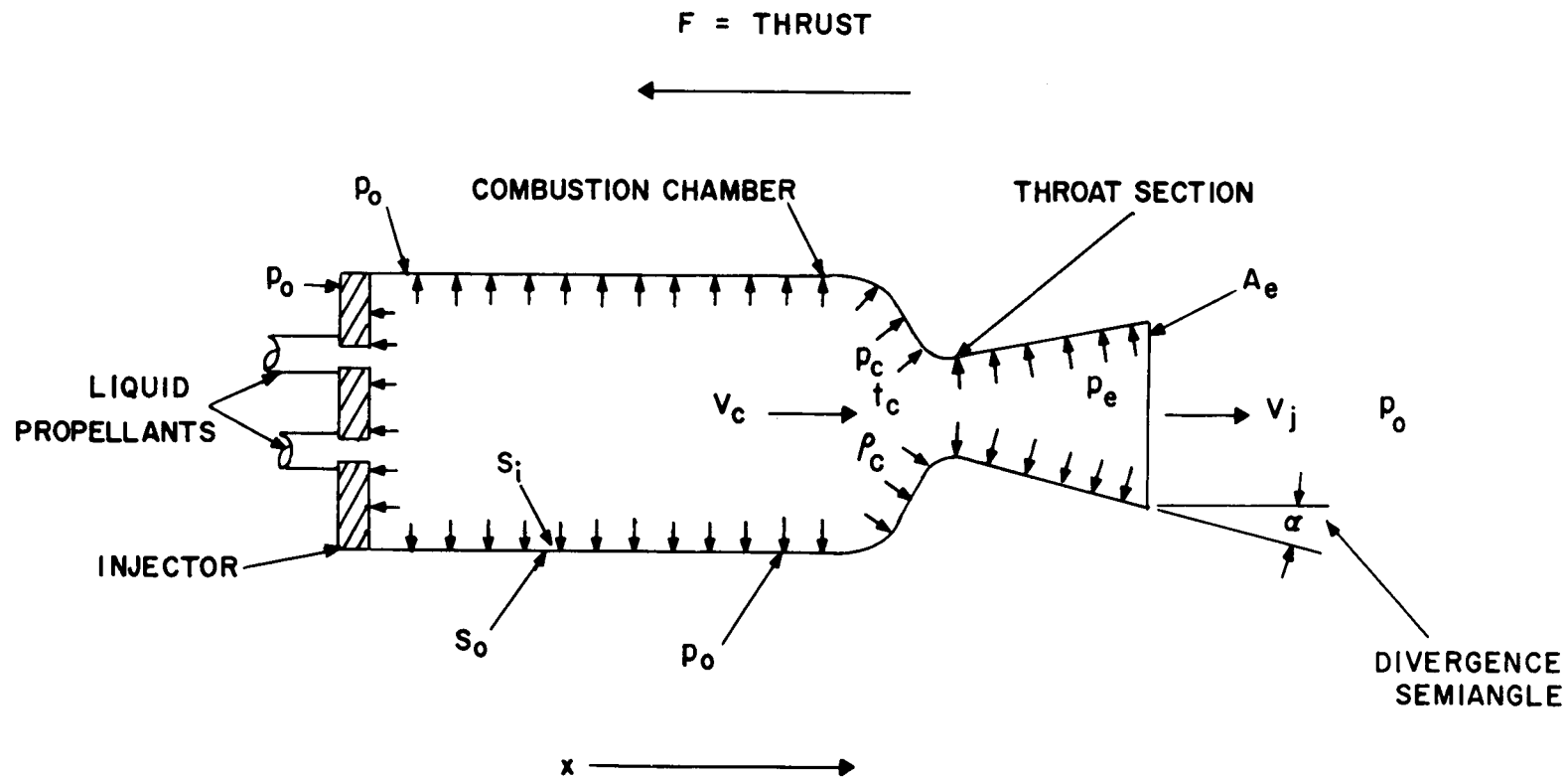
[2] Liquid propellants are discussed in Chapter 5.

[3] Solid propellants are discussed in Chapter 6.

high temperature, high pressure gases by burning a solid material the principal ingredients of which are a fuel and an oxidizer. The ingredients may be present either in the molecular structure of the solid propellant or they may be separate chemical compounds which are present as a suitable physical mixture. Solid propellants may be segregated into double-base propellants, and composite or heterogeneous propellants.

2-3.1. Liquid Monopropellant Engines. A liquid monopropellant is a liquid which may be either a single chemical compound such as nitromethane, or a mixture of chemicals that contains all of the chemical elements for initiating a high-energy, gas-producing chemical reaction. A rocket engine which develops its thrust from the chemical reaction (usually a decomposition) of a liquid monopropellant is termed a liquid monopropellant engine.

A liquid monopropellant engine has the advantage of simplicity because a single liquid is involved. All of the liquid monopropellants investigated require the addition of energy to initiate the decomposition of the monopropellant. Ordinarily, that energy is supplied by a pyrotechnic igniter, an electrically heated glow plug, a spark plug, or a small supply of auxiliary fluid with which it reacts readily.

Among the liquid monopropellants that have been investigated are ethylene oxide, n-propyl nitrate, isopropyl nitrate, nitromethane, diethyleneglycol dinitrate, acetylenic compounds, mixtures of methyl nitrate and methyl alcohol, hydrazine, and mixtures of nitric acid with benzene and water.

A satisfactory liquid monopropellant is one which is stable under all storage conditions but which decomposes completely when it is injected into the combustion chamber of a rocket engine. In general, these requirements are conflicting and greatly restrict the choice of possible liquid monopropellants. As a rule, the larger the thrust output per unit weight of a liquid monopropellant the greater is its sensitivity to shock; that is, the more explosive is its nature. (6)

It is doubtful that a liquid monopropellant will be found that will give better performance than the best liquid bipropellants. Consequently, monopropellants will probably not be used in the

rocket engines of a ballistic missile. On the other hand, monopropellants are widely used as the means for generating the gases for powering the turbines that drive propellant pumps and auxiliary power supplies in ballistic missiles.

2-3.2. Liquid Bipropellant Engines. A bipropellant engine develops its thrust by reacting a liquid oxidizer or oxidant with a liquid fuel, thereby producing tremendous quantities of high temperature, high pressure gas. In principle, liquid bipropellants are less hazardous than liquid monopropellants from shock sensitivity and thermal stability standpoints. When separated, the fuel and oxidant are ordinarily incapable of releasing energy in an explosive manner. Bipropellants which ignite spontaneously when they come in contact with each other in the combustion chamber of the rocket engine are said to be hypergolic. Those which require an addition of energy to initiate the chemical reaction are said to be diergolic.

The number of known liquids which are suitable as fuels is almost limitless, but there are only a few liquids, possibly a dozen, which can serve as practical oxidizers. Even so, the number of possible liquid bipropellant combinations is quite large.

The principal liquid oxidizers are the nitric acids, white fuming nitric acid (WFNA), red fuming nitric acid (RFNA), stabilized (red) fuming nitric acid (SFNA)[1], liquid oxygen (LOX), high strength (80 to 100 percent H_2O_2) hydrogen peroxide (HTP), mixed oxides of nitrogen (MON), and liquid fluorine (LF).

The principal liquid fuels are the hydrocarbon fuels, such as jet engine fuels JP-4 and JP-5, aniline and mixtures of aniline with furfuryl alcohol, alcohol water mixtures, hydrazine, unsymmetrical dimethylhydrazine (UDMH), diethylenetriamine (DETA), anhydrous ammonia, and mixtures made of other fuels with either hydrazine or UDMH. A more detailed discussion of liquid propellants is presented in Chapter 5.

2-3.3. Double-Base Solid Propellants. (2, 5, 7) These consist primarily of gelatinized colloidal mixtures of nitrocellulose and nitroglycerin to which suitable plasticizers, ballistic modifiers, and stabilizers have been added. To this group of propellants belong such materials as ballistite and cordite. They are used most extensively for such weapons as artillery barrage rockets, bazookas, aircraft rockets, unguided ballistic missiles, etc. They are also used in the boosters for launching turbojet and ramjet propelled guided missiles.

Double-base propellants burn with little smoke and at ambient temperatures are hard and tough. When stored at temperatures continuously above approximately 120°F they tend to deteriorate.

Double-base propellant grains are made by extrusion (solventless extrusion for large grains, and solvent extrusion for the small grains), and by casting. Large double-base grains can also be made from smaller extruded sections by cementing them together in an appropriate manner.

2-3.4. Composite or Heterogeneous Propellants. (7) A composite propellant consists of an inorganic oxidizer, in powder form, thoroughly mixed with an organic fuel which also serves as the binder for the oxidizer particles. (8) Most of the composite propellant formulations can be cast directly into the case of the rocket motor. There are, however, some formulations which are employed for producing molded grains.

The composite type of propellant first used on a wide scale in this country was the castable asphalt-base propellant employed in JATO[2] units. It was a mechanical mixture of potassium perchlorate and asphalt, the latter serving as the fuel and also as the binder for the oxidizer. The powdered potassium perchlorate was mixed with molten asphalt and the mixture cast either directly into the motor case, the walls of which were covered with a suitable lining material (liner); or into a suitable mold for solidification, then removed and installed in the motor case. Because of its poor physical and ballistic properties, asphalt propellant is not suitable for ballistic missile applications.

Modern composite propellants use an elastomeric material as the binder which is mixed in monomer form with the oxidizer particles and then polymerized to form a rubber-like material. In most of the current castable composite propellant formulations the oxidizer is ammonium per-

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[1] The approximate composition of SFNA is 83 percent HNO_3, 14 percent NO_2, 2 percent H_2O, 1 percent HF.

[2] JATO—Jet Assisted Take Off.

chlorate. Some formulations include finely divided metals such as aluminum. It should be noted that in all composite propellants the binder (or fuel) comprises only approximately 20 percent by weight of the finished propellant, the balance being solids. Hence, to obtain a propellant (fuel and oxidizer) having a satisfactory tensile strength, the binder (fuel) must have a tensile strength several times that required for the propellant.

In addition to the main ingredients of oxidizer and fuel, a solid propellant generally contains small amounts of several other materials called additives, each of which has an influence upon either the control of the manufacturing process, the burning rate, the physical properties, or the storage stability. With some formulations a small change in the additives, either in the type or amount, can cause important changes in the properties of the propellant.

Several different configurations are used for making composite and double-base propellants. In certain grain designs one or more surfaces of the propellant grain are prevented from burning by applying an inhibitor, a material which is either inert chemically or burns at a much slower rate than the propellant, to those surfaces.

In several cases the composite propellant is cast directly into the case of the rocket motor, and is bonded to the inner wall of the casing by interposing a lining material between the grain and the wall. The liner adheres to both the metal wall and the propellant grain, and inhibits burning. This arrangement is known as case-bonding. It has the advantages of supporting the grain and protecting the metal casing from hot combustion gases. Consequently, the metal case may be designed on the basis of its cold strength, and may be thin and light in weight. (9) For case-bonding to be successful the coefficients of thermal expansion of the metal wall, the liner, and the propellant must be properly matched so there will be neither separation nor cracking of the liner with temperature changes and temperature cycling.

Solid propellant grains having inhibited surfaces are termed restricted-burning grains. A grain which burns only on its internal surface is called an internal-burning grain. Restricted-burning grains are used in applications where relatively long burning times are required, for example, in solid propellant motors for ballistic missiles.

Where it is desirable to produce a large thrust for a relatively short time, as in launching or boosting applications, a propellant grain configuration which allows burning of more than one surface of the grain is frequently used. Propellant grains having no inhibited surfaces are termed unrestricted-burning grains. Figure 2-7 illustrates several grain configurations that have been employed.

2-4. ESSENTIAL COMPONENTS OF LIQUID BIPROPELLANT ROCKET ENGINES

Since liquid monopropellants do not have the capabilities for giving the high performance required for a ballistic missile the following discussions are confined to liquid bipropellant rocket engines. An engine of the latter type comprises four main subassemblies:

1. tanks for storing the liquid oxidizer and the liquid fuel, hereafter termed the propellant tanks

2. one or more rocket motors, or thrust chambers, wherein the oxidizer and fuel are burned to produce very large quantities of hot gases

3. means for removing the propellants from the propellant tanks and forcing them into the combustion chamber of the rocket motor against the combustion pressure (the propellant pressurizing system)

4. means for controlling the operation of the engine so that it performs in the desired manner and also protects against disaster in the event of malfunction.

Only items 2 and 3 will be discussed.

In general, the requirements imposed upon a liquid rocket engine depend upon the application. In many cases the application requires that the performance of the engine be independent of the temperature of the liquid propellants over the range −65°F to 160°F. Since the physical properties of practically all chemicals vary with their temperature the number of liquid chemicals that can satisfy the temperature requirements is quite limited. As a consequence, one finds that a large portion of the engineering effort in developing a new liquid rocket engine is devoted to making the engine operate satisfactorily and reliably over a wide range of temperatures. Perhaps the costliest and most time-consuming part of liquid

engine development is that concerned with obtaining reliable operation at very low temperatures (below −20°F). In view of the foregoing, the specifications for the required range of operating temperatures should not be made any wider than is warranted from a realistic appraisal of the conditions under which the rocket propelled ballistic missile is to be used. Furthermore, wherever it is practicable, means should be provided for protecting the propellant (or propellants) against cold weather (such as heating blankets).

2-4.1. Thrust Chamber. Figure 2-3 illustrates schematically the essential elements of a liquid bipropellant rocket engine.
They are:

1. the injector, for introducing the propellants into the combustion chamber and for metering their flow rates
2. the combustion chamber, wherein the chemical reaction occurs
3. the De Laval exhaust nozzle (converging-diverging nozzle) for expanding the combustion gases to give a supersonic jet velocity.

In addition to the above there are the pertinent valves and pressure regulating devices. If the propellants are diergolic (see paragraph 2-3.2) some form of ignition system must be provided. This may be an electrically heated glow plug, a spark plug, a small quantity of fuel which is hypergolic with the oxidizer leading the main fuel, or a pyrotechnic igniter having a burning duration of a few seconds. (5)

2-4.1.1. The Injector. The injector is ordinarily located at the fore end of the rocket engine. Its function is to introduce the propellants into the combustion chamber through several injection orifices, and to meter, atomize, and mix them so they will burn smoothly and release their maximum thermochemical energy. If $\dot{W}_o$ and $\dot{W}_f$ denote the oxidizer and fuel flow rates respectively, then the mixture ratio is $r = \dot{W}_o/\dot{W}_f$. $\dot{W}_o$, $\dot{W}_f$, and r depend upon the areas of the injection orifices A, their discharge coefficients C_d, and the differential pressures Δp acting upon them. In general, the weight rate of flow of an incompressible fluid $\dot{W}$, having the specific weight γ, is given by

$$\dot{W} = C_d A \sqrt{2g\gamma\Delta p} \qquad (2\text{-}1)$$

Hence, the mixture ratio r is given by

$$r = \frac{\dot{W}_o}{\dot{W}_f} = \frac{(C_d)_o A_o}{(C_d)_f A_f} \sqrt{\frac{\gamma_o \Delta p_o}{\gamma_f \Delta p_f}} \qquad (2\text{-}2)$$

The subscripts o and f refer to the oxidizer and fuel orifices respectively.

Since the discharge coefficients $(C_d)_o$ and $(C_d)_f$ are functions of the Reynolds number, the orifices should be selected so they operate in a range where their discharge coefficients do not vary appreciably over the expected range of variation in the Reynolds number.

In some injector designs an effort is made to aid the processes of mixing and atomizing the liquids, by causing the jets of oxidizer and fuel discharged from the injection orifices to impinge upon each other. Figure 2-4 illustrates schematically the principal configurations of the fluid jets used in the injectors for liquid bipropellant rocket engines.

No rational principles have been formulated for scaling injectors or predicting their combustion performance. Injector development is a costly, time-consuming, empirical process, which depends upon experience combined with trial and error. In fact, the problems concerned with scaling liquid bipropellant rocket engines are primarily injector problems. Much research effort will have to be expended if rational principles for scaling injectors are to be developed.

2-4.1.2. The Combustion Chamber. The combustion chamber (see Figure 2-3) is that portion of the rocket motor wherein the propellants are burned. Ordinarily, the combustion pressure is between 300 and 1000 psia. The combustion chamber must be of sufficient volume for completing the processes of atomizing, mixing, igniting, and burning the liquid propellants by the time the gases arrive at the entrance to the exhaust nozzle. The stay, or residence time for propellants in the combustion zone (a region which is not well defined) depends upon the volume of the combustion chamber. In general, the more reactive the propellants the smaller the required stay time. Since the rate of reaction increases with the combustion pressure, increasing the combustion pressure reduces the necessary stay time, other conditions being equal.
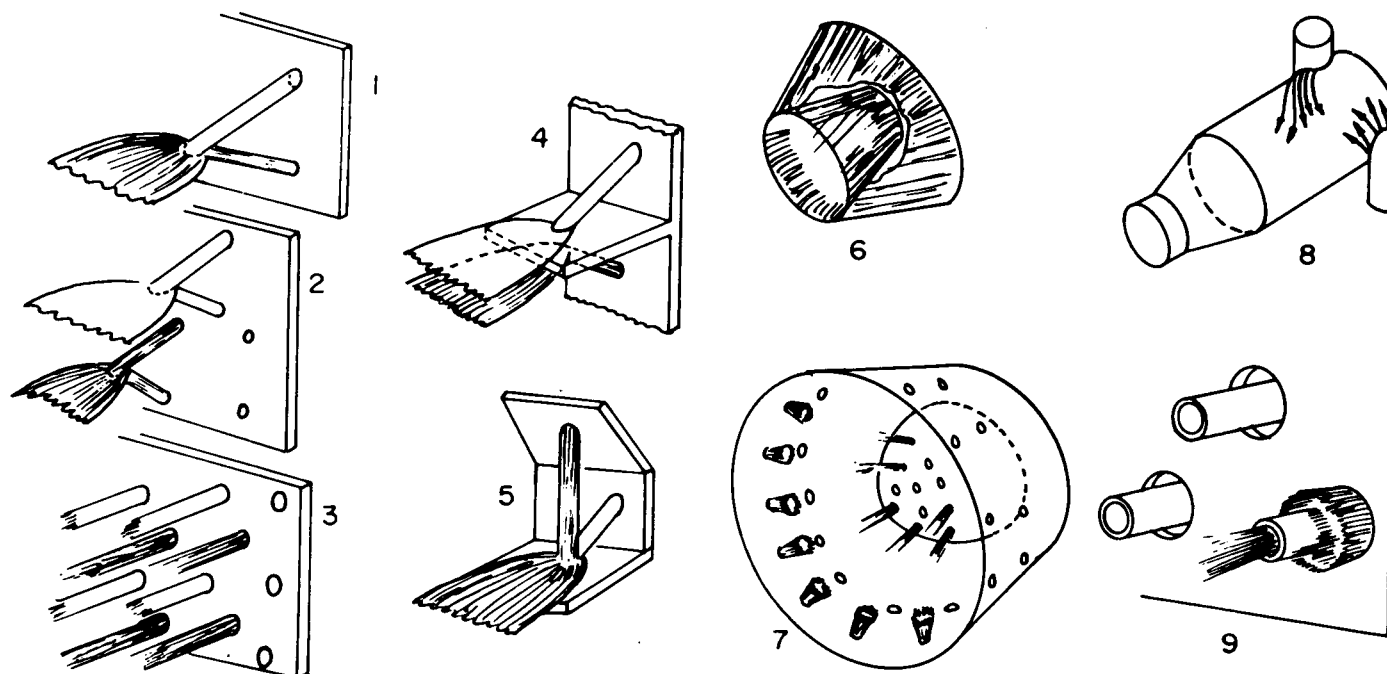
(1) Unlike impinging. (2) Like-on-like impinging. (3) Nonimpinging (showerhead).
(4) Splash plate. (5) Mix plate (Enzian). (6) Converging-diverging cones.
(7) Intersecting cones and jets (V-2 Rosette) with O_2 in center. (8) Premix. (9) Coaxial.

(Taken from Reference 12)

Figure 2-4. Configurations of Fluid Jets Used in Liquid Bipropellant Injectors

PROPULSION AND PROPELLANTS

Conditions in the combustion chamber are quite complex. At the injector there is a high degree of heterogeneity, since the liquids are being injected into turbulent hot gases. At the nozzle end, assuming complete combustion, only gases are flowing downstream. Consequently, there is a small pressure gradient in the direction of the gas flow, signifying that the pressure, density, temperature, and velocity of the gases vary from the injector to the nozzle end. (10)

Because weight is at a premium in the case of vehicles such as ballistic missiles it is essential that the combustion chamber be of the smallest size that will give the required stay time for completing the combustion of the propellants. It can be shown that a practical parameter which is a measure of the stay time is the so-called characteristic length L^*, which is defined by, (1, 5, 11)

$$L^* = \frac{\text{Volume of combustion chamber}}{\text{Area of throat of the exhaust nozzle}} \quad (2\text{-}3)$$

In calculating the value of L^* for a motor it is customary to include in the combustion volume all of the volume between the injector face and the throat section of the nozzle. The minimum usable value of L^* is determined experimentally.

In the case of high performance, relatively long duration engines such as those employed for propelling ballistic missiles, the interior surfaces of the thrust cylinder must be cooled. Current practice is to use either the oxidizer or the fuel as a coolant before it is injected into the thrust cylinder. This method of cooling is termed regenerative cooling. (13, 16) With regenerative cooling it can be assumed that there is no loss of heat from the system. It is essential that the cooling load imposed upon the regenerative coolant be smaller than that which will cause it to boil in the coolant passages. (13) The combustion chamber should, therefore, be designed so that its surface exposed to the hot combustion gas is the smallest compatible with the required value of L^* for best performance.

2-4.1.3. The Exhaust Nozzle.

The throat area of the exhaust nozzle determines the combustion pressure, the rate at which propellants are consumed, and the thrust. It is essential that the nozzle be cooled adequately. Experiments show that the overall heat flux for the nozzle is approxi-

mately 3 to 4 times that for the combustion chamber. (14, 15) The critical region is the throat section where the heat flux is between 3 and 4 times the overall value for the nozzle. In some cases it may be necessary to augment regenerative cooling of the throat section with some form of internal cooling such as film cooling. (16, 17)

2-4.2. Means for Pressurizing Liquid Propellants.

There are three principal systems for forcing liquid propellants from the propellant tanks into the thrust cylinder: stored gas pressurization, chemical gas pressurization, and turbopump pressurization.

2-4.2.1. Stored Gas Pressurization.

Figure 2-5 illustrates schematically the principal elements of a stored gas pressurizing system. A gas such as nitrogen or helium is stored under pressure (1800 to 3000 psia) and used for pressurizing the propellant tanks. The system is simple and reliable. Gas is supplied to the propellant tanks at a regulated pressure which maintains the propellant flow rates at the desired values. The gas pressure in each propellant tank exceeds the combustion pressure by the sum of the pressure drops in the propellant feed line and the injector. Consequently, the propellant tanks must be designed to withstand relatively high pressures.

It is essential that the pressurizing gas shall not react chemically with, or dissolve in, either the fuel or the oxidizer. Where one or both of the propellants is a liquefied gas, such as liquid oxygen, the pressurizing gas must not condense when it comes in contact with the liquefied gas.

The stored gas pressurizing system is most applicable to either short-duration or small thrust rocket engines because of the large weights of the high pressure tanks for the stored gas and for the propellants. It may find application to ballistic missiles of relatively short range (up to approximately 75 mi) where simplicity and reliability are more important than missile weight.

The weight of pressurizing gas required for a given set of operating conditions depends upon the molecular weight and specific heat ratio for the stored gas. (5) Thus, the weight of helium required in a given case, compared to air or nitrogen, is approximately 65 percent. The decrease in the weight of stored gas achieved by using
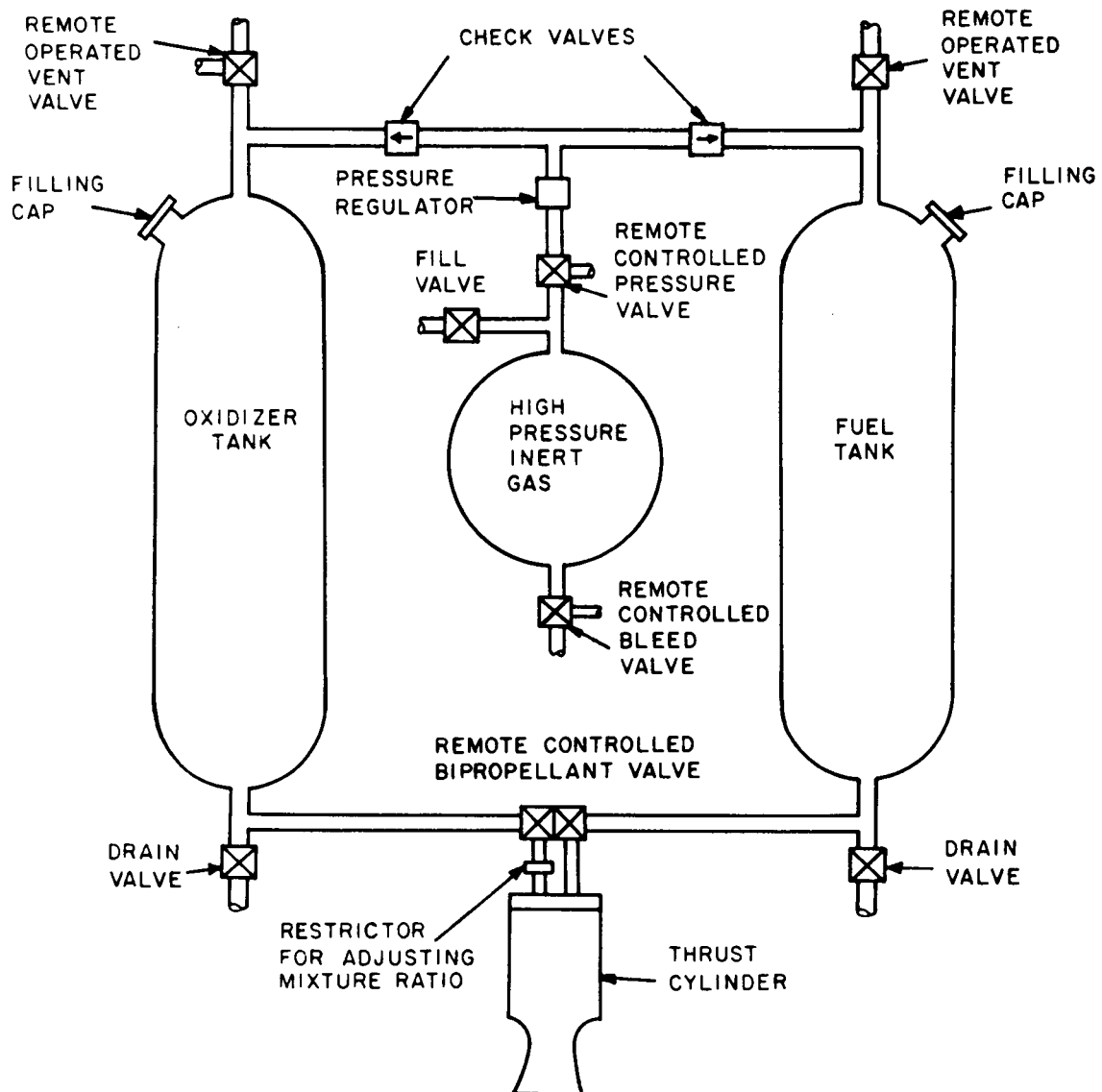
Figure 2-5. Stored Inert Gas Pressurization System for a Liquid Bipropellant Rocket Engine

PROPULSION AND PROPELLANTS

helium has an insignificant effect, however, on the weight of the pressurizing system because the weights of the stored gas and propellant tanks are practically unchanged.

2-4.2.2. Chemical Gas Pressurization. In this system the pressurizing gas is generated as it is used, thereby essentially eliminating the weight of the high pressure tank for storing the pressurizing gas. This gas is produced in a special generator either by reacting liquid bipropellants, or decomposing a monopropellant such as hydrazine, or by burning a solid propellant. Irrespective of the method employed, it is important that the pressurizing gas shall not react either chemically or physically with the liquid propellants. Moreover, the gas temperature must be low enough to preclude structural problems due to heating.

Low temperature gases which will not react chemically with the propellants can be obtained by employing two gas generators; one for pressurizing the oxidizer, and the other the fuel. The former is operated rich in oxidizer and the latter rich in fuel.

2-4.2.3. Turbopump Pressurizing System. The weight limitations of either the stored gas or the chemical gas pressurizing systems are removed by employing a turbopump pressurizing system. This consists of propellant pumps driven by a turbine which is powered by gases produced in some form of gas generator, as illustrated in Figure 2-6. As the thrust of the rocket engine is increased, there is a reduction in the operating duration for which the turbopump pressurizing system becomes lighter than the inert gas pressurizing system; for example, for a 5000 lb thrust engine the operating duration is approximately 25 sec and for a 50,000 lb thrust engine it is approximately 7 sec. Turbopump pressurization is particularly suitable in the case of liquid rocket engines which must develop either large thrusts, or operate for long durations, or both. This type of engine is particularly adaptable to the propulsion of intermediate and long range ballistic missiles.

Because of the importance of low weight in the liquid propellant engines for ballistic missiles, the turbines and pumps must be light in weight. Small turbines and pumps are generally operated at high speeds in order to hold weight to a

minimum. The pumps are usually centrifugal pumps with radial bladed impellers of high specific speed design and operate with high fluid velocities at their entrance sections. (18, 19, 20) To avoid cavitation, which occurs when the static pressure in the flowing fluid is smaller than its vapor pressure, the propellants must be pressurized. (21) Hence, the selection of the pump speed requires optimization of two influences: 1. the decreasing weight of higher speed pumps, and 2. the increasing weight of the gas pressurizing apparatus required for minimizing cavitation effects.

In most turbopump systems the gases for operating the turbine are produced in a separate gas generator either by reacting suitable propellants or by decomposing a monopropellant. The gases must be supplied at a temperature which the turbine blades can safely withstand.

In cases where the propellants burned in the gas generator are the same as those burned in the thrust cylinder, the mixture ratios must be either fuel-rich or oxidizer-rich in order to limit the gas temperature to approximately 1800°F. If the fuel is a hydrocarbon and the gases are fuel-rich, problems due to carbon depositing in critical passages of the gas generator and turbine are apt to be encountered. If the gases are oxidizer-rich severe corrosion problems may be met.

Gases produced by decomposition of high strength peroxide (HTP) for operation of the turbine consist of steam and oxygen at less than 1000°F.

2-5. ESSENTIAL COMPONENTS OF SOLID PROPELLANT ROCKET MOTORS

Usually the design of a solid propellant is hampered by the need for satisfying certain dimensional, weight, burning time, and performance specifications. To meet them the designer has the freedom of specifying the propellant formulation, the configuration of the propellant grain, and the method of supporting it in the rocket motor. (22) That freedom gives a great deal of flexibility to the design of solid propellant grains. By optimizing the combination of these variables the maximum performance is obtained. (23)

The general features of a solid propellant rocket motor were presented in paragraph 2-1. It is seen that the essential components of such a motor are:
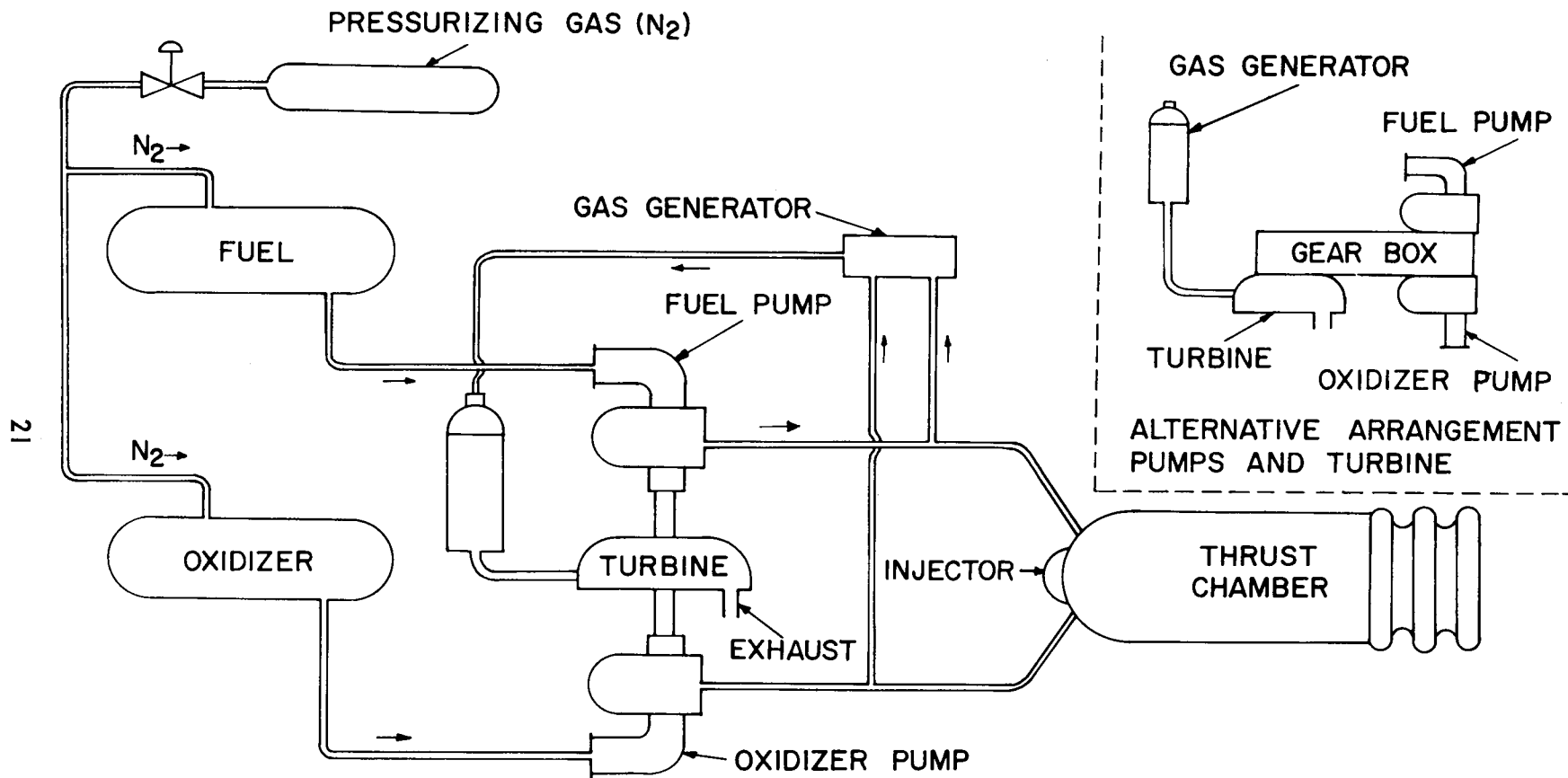
Figure 2-6. *Schematic Diagram of a Turbopump Arrangement for Pressurizing a Liquid Bipropellant Rocket Engine*

PROPULSION AND PROPELLANTS

2-5.1. Solid Propellant Grain Configurations.

The burning of a solid propellant surface occurs in parallel layers. If one assumes a constant area for the nozzle throat A_t, the relation between the combustion pressure p_c and the area of the burning surface S_p, then (2)

$$p_c = \text{constant} \left(\frac{S_p}{A_t} \right)^{1/(1-n)} \qquad (2\text{-}4)$$

the quantity n is called either the burning rate exponent or the pressure index, and is always less than unity. If the ratio S_p/A_t remains constant during the burning period, then p_c remains constant.

Since $1/(1-n)$ may have values ranging from approximately 1.67 to 5.0 it is clear that a small change in the burning area can cause large changes in the combustion pressure. In the case of solid propellant rockets for ballistic missiles, as well as for most other applications, it is desirable that the combustion pressure remain sensibly constant during the burning period.[1]

Grain design is based on obtaining the burning characteristics to give the desired curve of combustion pressure p_c as a function of the burning time τ_b. A grain which burns so that p_c does not vary with time, is said to give neutral burning; one for which p_c increases with τ_b gives progressive burning; and one for which p_c decreases with τ_b gives regressive burning. Most grain configurations are based on shapes which intrinsically give either neutral burning or progressive burning.

If A_G denotes the cross-sectional area of the propellant grain and A_C that of the case surrounding it, then

$$\epsilon_p = \frac{A_G}{A_C} = \text{the propellant loading ratio} \qquad (2\text{-}5)$$

To obtain the high performance required for ICBM and IRBM missiles the propellant loading ratio should be approximately 0.90.

The cross-sectional area of the flow passage through which the combustion gases flow past the burning surface or surfaces of the propellant

grain is termed the port area, and is denoted by A_P. Thus

$$A_P = A_C - A_G = \text{port area} \qquad (2\text{-}6)$$

If A_t denotes the area of the throat of the exhaust nozzle, then

$$\epsilon_{pt} = \frac{A_P}{A_t} = \frac{A_C - A_G}{A_t} = \text{port-to-throat ratio} \qquad (2\text{-}7)$$

Figure 2-7 illustrates schematically some typical solid propellant grain configurations.

2-5.1.1. End-Burning (Cigarette-Burning) Grain.

Figure 2-7a illustrates this type of grain. It is a restricted-burning (inhibited) grain and gives neutral burning; the burning surface recedes parallel to itself with no change in area. The asphalt-base propellants used in JATO units were end-burning grains. In the earlier designs the end-burning grain was bonded to the case with a rubbery pitch liner, while in later designs the circumferential surface and the bottom end were inhibited from burning and the grain was supported in the case with an annular space between the case and the grain.

2-5.1.2. Single-Perforated or Tubular Grain.

Figure 2-7b illustrates this grain configuration. The ends of the grain are inhibited from burning, so that the length of the grain remains constant during the burning period. Since the linear burning rates for the inner and outer burning surfaces may be assumed to be equal, the inner diameter of the grain d_i increases at the same rate that the outer diameter d_o decreases, as a consequence the grain gives neutral burning. The difference $d_o - d_i = 2w_t$, where w_t is called the web thickness of the grain. The duration of burning is controlled by w_t.

If the outer surface (including the end surfaces) of a single perforated grain is inhibited from burning, then burning occurs only on the inner surface. Such a grain is called an internal-burning tubular grain and gives progressive burning.

2-5.1.3. Case-Bonded Internal Burning Star Grain.

Figure 2-7c illustrates this form of grain. It is a development from the case-bonded internal burning tubular grain. The internal star configuration has great design flexibility since the

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[1] For a detailed discussion of the burning characteristics of solid propellants, see Chapter 6.

BURNING SURFACE   CASE

(a)
END
BURNING

GRAIN SUPPORT

(b)
TUBULAR

(c)
INTERNAL
BURNING
STAR

(d)
ROD AND
TUBE

SUPPORT ROD

(e)
CRUCIFORM

LEGEND

CHARGE
RESTRICTION (INHIBITOR)
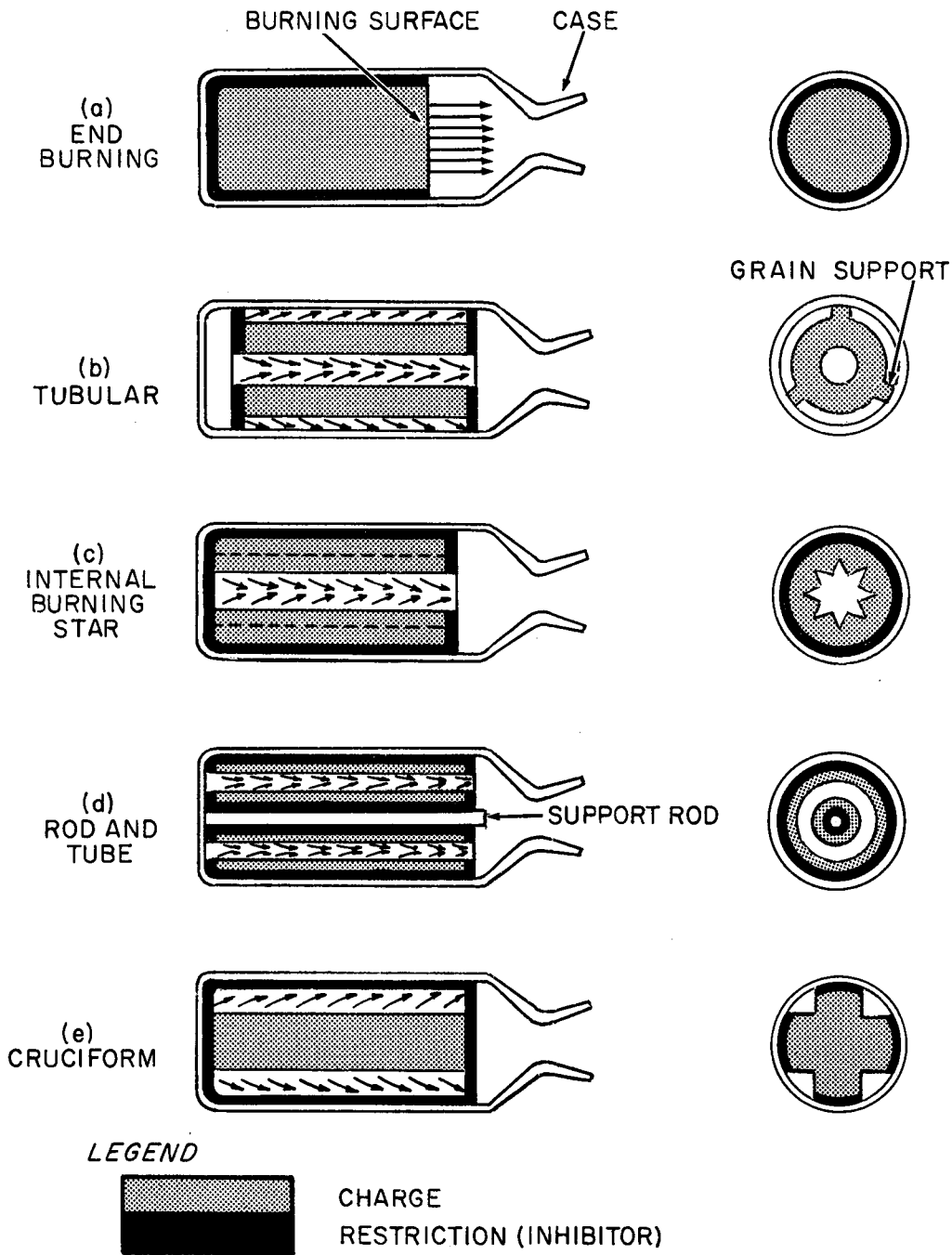
(Taken from Reference 7)

Figure 2-7. Typical Solid-Propellant Grain Configurations

number of star points, the star diameter, the angles of the star points, and web thickness can be varied by the designer. The grain can be designed so it gives either neutral burning, progressive burning, or regressive burning, and the case-bonding provides strong support for the grain and protects the case from the hot combustion gases. This grain configuration is widely used in large solid propellant rocket motors of the type suitable for propelling ballistic missiles.

2-5.1.4. Rod and Tube Grain. Figure 2-7d illustrates the rod and tube grain. The burning surfaces are the exterior surface of the rod and the internal surface of the tube, the latter being case-bonded. As burning proceeds the burning area of the rod decreases and that of the tube increases, and if their burning rates are equal, neutral burning can be obtained. By using different propellant formulations for the rod and the tube the pressure-time curve can be controlled within practical limits to give any desired variation of the combustion pressure as a function of time.

2-5.2. The Case or Housing. The case comprises a closed fore cap, an aft cap to which the exhaust nozzle is attached, and a motor tube which connects the fore and aft caps. Considering only case-bonded motor designs (since they are most appropriate for ballistic missiles), the fore cap and the motor tube can be of light weight construction because they are protected from the hot combustion gases. To keep the weight of the aft cap to a reasonable value the interior of that part is covered with an insulating material. Since there should not be any permanent deformation of the casing after it has been subjected to the hydrostatic test which is normally specified, the stress during that test should not exceed the yield point of the material. Since the cold strength of the chamber can be used for design purposes, the design condition is selected so that the stress in the material is equal to its yield stress at the maximum combustion pressure which may be expected, multiplied by a suitable factor of safety.

The criterion of material selection is the strength to weight ratio of the material. Currently, the most popular material for the metal parts is steel, such as heat treated 4130. Two promising

metals for rocket engine cases are aluminum alloy X7178, and 6Al-4V titanium alloy. Cases made from spun fiberglass bonded with an epoxy resin have been investigated experimentally and look promising. Table 2-1 compares the strength-to-weight ratios for three different metals.

TABLE 2-1. COMPARISON OF MATERIALS FOR SOLID PROPELLANT ROCKET CASES

(Reference 9)

Material	Min. Yield Strength (psi)	Specific Weight (lb/in^3)	Ratio of Strength to Specific Weight (in)
4130 Steel	150,000	0.285	527,000
	170,000	.285	596,000
	200,000	.285	700,000
X7178 Aluminum Alloy	82,000	0.100	820,000
6Al-4V Titanium Alloy	140,000	0.16	875,000
	160,000	.16	1,000,000

According to reference 9 , it should be possible with good design to achieve a ratio of propellant-to-engine weight of approximately 0.93.

2-5.3. The Exhaust Nozzle. In current designs the exhaust nozzle operates uncooled and its interior surfaces must be protected from the hot gases, particularly in the region of the throat. A composite construction is employed in many designs; the nozzle section in contact with the gases being made from carbon or some form of a ceramic. In most engines the weight of the nozzle is a substantial fraction of the total weight of the metal parts.

In the effort to reduce nozzle weight new materials and new high temperature insulating coatings and materials are being investigated. For a coating to be satisfactory it must have good adherence to the inner surface of the nozzle and good resistance to erosion.

2-5.4. The Igniter. The igniter for a solid propellant rocket usually comprises three main components: some form of electrically fired squib for initiating combustion, the main igniter charge, and the case. The squib consists of two lead wires which are insulated from each other and which are connected together by a fine high resistance wire. The latter is surrounded by an explosive or combustible material, called the primary charge,

which is sensitive to heat. When the wire is heated electrically the primary charge is ignited. Sufficient heat must be released by the primary charge to ignite the main igniter charge.

Various materials are used as the main igniter charge, from black powder to mixtures of metals with an oxidant such as potassium perchlorate. Metals which have been investigated in making main igniter charges are aluminum, boron, magnesium, and zirconium. (24)

It is essential that the igniter initiate the combustion of the solid propellant under the conditions expected in the actual operation of the rocket engine. Moreover, the ignition delay should be short and also reproducible. Since the speeds of the chemical reactions occurring in an igniter decrease with decrease in the absolute pressure, adequate precautions must be taken to insure that in the case of a multistage ballistic missile satisfactory ignition can be obtained at very high altitudes, for example, more than one hundred miles where the absolute pressure of the atmosphere is practically zero.

2-6. THRUST CUT-OFF AND THRUST VECTOR CONTROL

The range and accuracy of a rocket propelled ballistic missile are governed by the attitude of the missile and its velocity at the instant that the thrust is terminated. (See the Trajectories Volume of this series) It is important, therefore, that those variables have the correct values required for reaching the target. Consequently, all rocket engines for propelling ballistic missiles must incorporate means for achieving thrust termination, more commonly called thrust cut-off, at the correct instant. In addition, they must be equipped with controls for altering the direction of the line of action of the propulsive thrust. Means for achieving the latter are termed thrust vector control.

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Chapter 3

CRITERIA OF ROCKET ENGINE PERFORMANCE

3-1. THRUST EQUATION

When a rocket engine (liquid or solid fuel) is operated under steady conditions the variables p_c, t_c, ρ_c, and V_c do not change with burning time[1] (see Figure 2-3). The thrust developed by the rocket engine is the resultant axial component of the static pressure forces acting upon its interior and exterior surfaces. The static pressures acting upon the interior surfaces depend upon the rate at which propellants are burned, the thermochemical characteristics of the gases produced by their combustion, the area of the throat of the exhaust nozzle, and to a small extent upon the static pressure of the environment into which the combustion gases are ejected. In any case the internal static pressures are several times the external static pressures. If F denotes the thrust, and since, in general, the forces acting normal to the longitudinal axis of the thrust cylinder (the x-axis) do not contribute to the thrust, (1, 2) then

$$F = \int_{S_i} (p_i dS)_x + \int_{S_o} (p_o dS)_x \qquad (3-1)$$

where p_i = the static pressure acting on the interior surface of the rocket engine S_i

p_o = the atmospheric pressure acting on the exterior surface of the rocket engine S_o

x — denotes that the axial component (x-component) is to be evaluated.

It is difficult, if not impossible, in an actual case to evaluate the integrals in equation (3-1). The thrust F is, therefore, calculated by applying the momentum theorem of fluid mechanics to the gases flowing through the thrust cylinder (2) (see paragraph 3-1.3).

3-1.1. Velocity of Gases Crossing Exit Section of Nozzle. Figure 3-1 illustrates the thermodynamic conditions for a liquid bipropellant rocket engine and a solid propellant rocket motor with an end-burning grain. The combustion gases arrive at the entrance section of the exhaust nozzle with the static pressure p_c, the static temperature t_c, and the velocity V_c. In flowing through the exhaust nozzle the gases are expanded, and they arrive at the exit section of the nozzle, having the cross-sectional area A_e, with the velocity V_e, and the thermodynamic properties p_e and t_e. The kinetic energy associated with the jet gases is $V_e^2/2g$. If h_c denotes the static specific enthalpy of the gases entering the exhaust nozzle in Btu/lb, and V_c their velocity in ft/sec, then

$$h_c + \frac{V_c^2}{2gJ} = H_c = \text{stagnation specific} \quad (3-2)$$
enthalpy of gases entering exhaust nozzle (in Btu/lb).

The exhaust velocity V_e is accordingly[2]

$$V_e = [2gJ(H_c - h_e)]^{1/2} \approx [2gJ(h_c - h_e)]^{1/2} \qquad (3-3)$$

where J = the mechanical equivalent of heat = 778 ft-lb/Btu.

3-1.2. Nozzle Divergence Coefficient. Only the x-component (see Figure 3-1) of the velocity V_e, denoted by V_{ex}, contributes to the thrust developed by the thrust cylinder. If λ is the divergence coefficient for the nozzle, then

$$V_{ex} = \lambda V_e \qquad (3-4)$$

If α denotes the semi-divergence angle of the exhaust nozzle (usually between 12 and 20 deg), then (3)

$$\lambda = \frac{1}{2} + \frac{1}{2}\cos\alpha = \text{divergence coefficient} \quad (3-5)$$
of the exhaust nozzle.

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[1] Steady conditions are assumed in all of the discussions unless otherwise specifically stated.

[2] Since V_c is ordinarily quite small compared to V_e, the static values of the thermodynamic properties will be employed.

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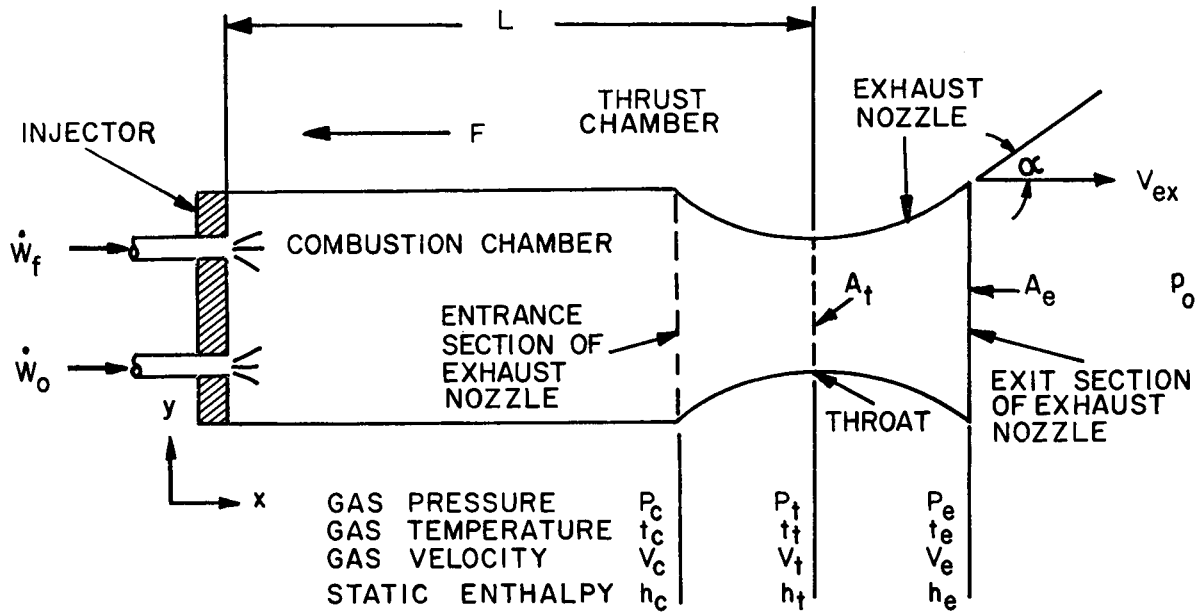
(a) Liquid Propellant Rocket Engine
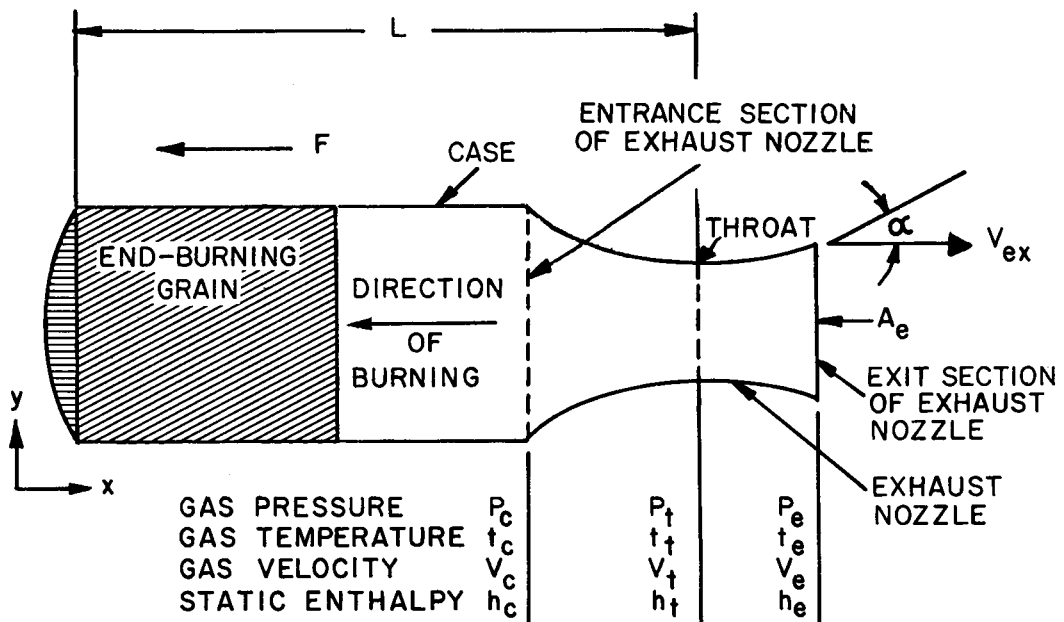
(b) Solid Propellant Rocket Motor with End-Burning Grain

(Taken from Reference 2)

Figure 3-1. Thermodynamic Conditions for Liquid and Solid Propellant Rockets

To calculate the performance of a propellant system it is necessary to 1. calculate the combustion temperature t_c corresponding to p_c, and 2. calculate the exhaust velocity V_e.

3-1.3. Calculation of Thrust by Momentum Theorem.

The momentum theorem of fluid mechanics states that *the time rate of change of a bounded mass system of discrete particles (a body of fluid for example) in any direction is equal to the resultant of the external forces acting on the boundaries in the specified direction and is independent of the internal forces.* (2) The mathematical statement of this principle is

$$\Delta \underset{\sim}{M} = \int_{\tau=1}^{\tau=2} \sum F_{ext} \, d\tau \qquad (3\text{-}6)$$

where

$\Delta \underset{\sim}{M}$ = the change in momentum of the body of fluid.

$F_{ext} \, d\tau$ = the time impulse of the external force F_{ext}.

Figure 3-2 illustrates the case where an arbitrary propulsion system propels a vehicle through a fluid medium with the flight speed V_o. For convenience a relative coordinate system is employed; the vehicle and its engine are assumed to be stationary and the fluid flows toward them with the velocity V_o. The infinite planes S_a and S_b are perpendicular to the longitudinal axis of the system; the latter axis is parallel to the x-axis. The plane S_a is located far enough from A_1 so that $p_1 = p_o$ = the undisturbed atmospheric pressure. Plane 2 is located so that $p_2 = p_o$ except for the area A_e crossed by the jet. It can be shown that if X is the force acting on the gases flowing through the engine, the action force causing the velocity to increase from V_o to V_1; then the thrust F, the reaction force, is, in general, given by (1, 2)

$$F = |X| = \dot{m}_2 V_2 - \dot{m}_1 V_o + (p_e - p_o)A_e \qquad (a)$$

In the case of a rocket engine, since it consumes no air, the entrance momentum flux $\dot{m}_1 V_o = 0$. For a rocket engine

$$\dot{m}_2 = \dot{m} = \dot{m}_o + \dot{m}_f \qquad (b)$$

From equation (3-4)

$$V_2 = V_{ex} = \lambda V_e \qquad (c)$$

Hence

$$F = \dot{m}\lambda V_e + (p_e - p_o)A_e \qquad (3\text{-}7)$$

Equation (3-7) shows that the thrust is composed of two parts

(a) the momentum thrust $(\dot{m}\lambda V_e)$, and

(b) the pressure thrust $(p_e - p_o)A_e$

Since the momentum thrust is ordinarily several times the pressure thrust, the thrust developed by a rocket engine is primarily a function of the mass rate of flow (consumption) of propellants. It is apparent from equation (3-7) that under the assumed steady operating conditions p_c and p_e are constants, so that the thrust increases with the operating altitude of the rocket engine, or decreasing values of p_o, and that the maximum thrust is obtained when $p_o = 0$.

It is common practice in rocket engineering to express the thrust in terms of the weight rate of propellant consumption $\dot{W} = \dot{m}g$. Thus

$$F = \frac{\dot{W}}{g_o}\lambda V_e + (p_e - p_o)A_e \qquad (3\text{-}7a)$$

where $g_o = 32.174 \text{ ft/sec}^2$.

3-2. SPECIFIC IMPULSE

The performance obtained by burning the propellants in a rocket engine is expressed in terms of the specific impulse, which is denoted by I_s. Thus (2, 4, 5)

$$I_s = \frac{F}{\dot{W}} = \frac{1}{W_p}\int F d\tau \qquad (3\text{-}8)$$

where W_p is the total weight of propellants consumed (based on constant gravitational attraction) in the time $\int d\tau$, and $\dot{W} = dW/d\tau$ = the corresponding weight rate of propellant consumption.

The units for I_s based on equation (3-8) are seconds. It must be kept in mind, however, that I_s is independent of the value of gravity. For that reason, I_s is sometimes defined by (4)

$$I_s = \frac{F}{\dot{W}}\left(\frac{g}{g_o}\right) \qquad (3\text{-}9)$$

where g is the local acceleration due to gravity and g_o is the standard gravitational acceleration (32.1740 ft/sec²).

If I_s is defined by $F/\dot{m}$, as is sometimes done, then its dimensions are $(ML/T^2)/(M/T) = L/T$.
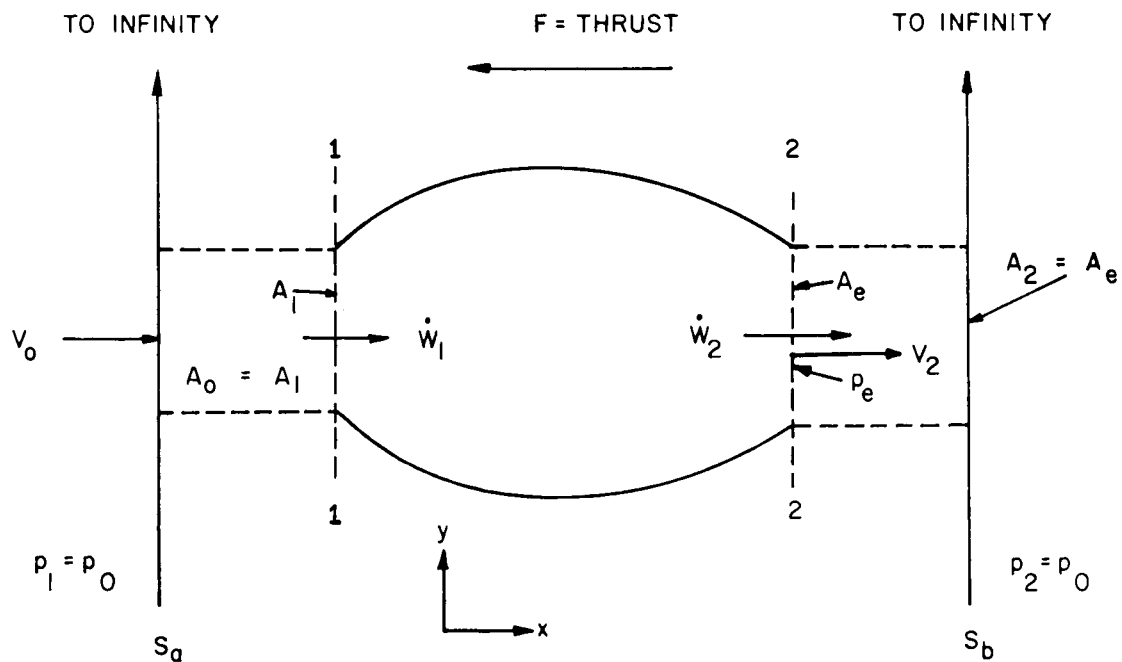
Figure 3-2. Application of the Momentum Theorem of Fluid Mechanics to an
Arbitrary Propulsion System
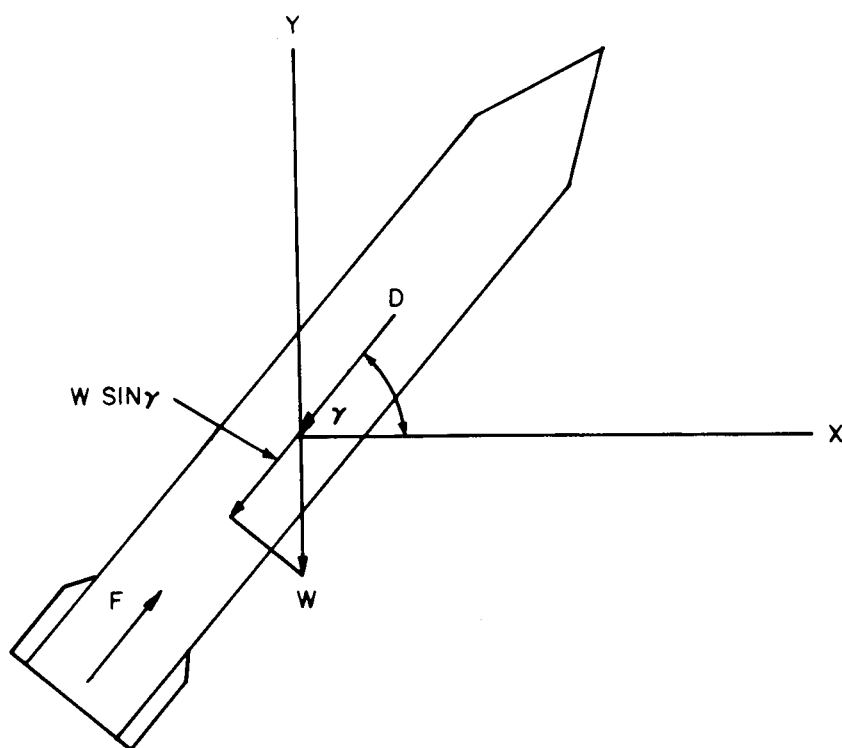
Figure 3-3. Free Body Diagram for a Rocket Propelled Ballistic Missile

Equation (3-8) is, however, the most widely used definition for I_s.

The specific impulse I_s is basically a property of the propellants burned in the rocket engine. For any given solid propellant formulation, or specific liquid fuel and liquid oxidizer system, a theoretical value for the specific impulse can be calculated by applying the methods of thermochemistry to the chemical reaction and to the expansion process. The specific impulse obtained from thermochemical calculations will be called the theoretical specific impulse and denoted by I'_s.

In the case of a solid propellant rocket motor the instantaneous rate of propellant consumption $\dot{W}$ cannot be measured. The measured specific impulse I_s is an average value calculated from the curve of thrust versus burning time (thrust-time curve) and the weight of solid propellant consumed during the burning period.

3-3. TOTAL IMPULSE

If the thrust-time curve obtained from firing a rocket engine is integrated over the burning duration, the result is called either the total impulse or briefly the impulse, and is denoted by I. Thus

$$I = \int_o^{\tau_b} F d\tau = I_s \dot{W} \tau_b = W_p I_s \text{ (lb-sec)} \quad (3\text{-}10)$$

It follows from equation (3-10) that if all other factors remain unchanged for a given rocket engine, the same total impulse can result from a small thrust over a long time or from a large thrust over a short time.

3-4. EFFECTIVE JET VELOCITY

In a static firing test of a rocket engine (liquid or solid) the thrust F is readily measured. Also the average rate at which the propellants are consumed W_p/τ_b can be determined with a high degree of accuracy. It is very difficult, however, if not practically impossible, to make an accurate measurement of the exit pressure p_e (see Figure 3-1). It is convenient, therefore, to introduce a fictitious velocity V_j, called either the effective jet velocity or the effective exhaust velocity, so that the following simple equation can be written for the thrust. Thus

$$F = \dot{m} V_j = \frac{W}{g} V_j \quad \text{(lb)} \quad (3\text{-}11)$$

From equations (3-7) and (3-11) it follows that if the exhaust nozzle operates with complete expansion ($p_e = p_o$), then

$$V_j = \lambda V_e = V_{ex} \quad (3\text{-}12)$$

It should be borne in mind that from the firing test of a rocket engine it is the effective jet velocity V_j and not the exit velocity V_e that is computed.

By means of equations (3-8) and (3-11) it is readily shown that

$$V_j = g \frac{F}{W} = g I_s \quad (3\text{-}13)$$

The weight of propellants consumed in developing an impulse of 1 lb-sec is called the specific propellant consumption and is denoted by $\dot{W}_s$. Thus

$$W_s = \frac{1}{F}\left(\frac{W_p}{\tau_b}\right) = \frac{\dot{W}}{F} = \frac{1}{I_s} = \frac{g}{V_j} \quad (3\text{-}14)$$

3-5. THRUST COEFFICIENT

When a rocket engine is fired on the test stand it is relatively easy to measure accurately the combustion pressure p_c, the thrust F, the nozzle throat area A_t at the beginning and end of the run, and the propellant consumption rate $\dot{W} = F/I_s$. The aforementioned variables are related by

$$F = C_F p_c A_t = \dot{W} I_s \quad (3\text{-}15)$$

from which one obtains

$$C_F = \frac{F}{p_c A_t} = \text{the thrust coefficient} \quad (3\text{-}16)$$

Strictly speaking the value of A_t that should be used in equation (3-15) is the throat area during the firing run. Since that area cannot be measured, the value of A_t used in the equation is one that is estimated from the value of A_t measured prior to the firing run and the temperature of the nozzle material.

Curves of C_F as a function of p_c obtained experimentally for several different mixture ratios $r = \dot{W}_o/\dot{W}_f$ and for different propellant combinations, comprise the basic data for establishing the throat area of the exhaust nozzle. When experimental data are unavailable, theoretical values of C_F, denoted by C'_F, can be calculated by thermodynamic methods (see paragraph 4-5.5).

3-6. WEIGHT FLOW COEFFICIENT

It is convenient to express the propellant consumption rate $\dot{W}$ in terms of p_c, A_t, and a weight flow coefficient C_w. Thus

$$C_w = \frac{\dot{W}}{p_c A_t} \qquad (3\text{-}17)$$

For a given propellant combination it is customary to obtain experimental curves of C_w as a function of p_c from firings of small rocket engines. The curves give the information required to predict the propellant consumption rate for developing any specified thrust with those propellants.

From equations (3-15) and (3-17), it is seen that C_F and C_w are related to I_s by

$$I_s = \frac{C_F}{C_w} \qquad (3\text{-}18)$$

3-6.1. Mass Flow Coefficient. In a manner similar to equation (3-17), a mass flow coefficient, denoted by $C_{\dot{m}}$, can be defined. Thus

$$C_{\dot{m}} = \frac{\dot{m}}{p_c A_t} \qquad (3\text{-}19)$$

where $\dot{m}$ is the mass rate of propellant consumption.

3-7. CHARACTERISTIC VELOCITY

The characteristic velocity denoted by c^* is frequently employed for comparing the performance of different rocket engines. This parameter measures the effectiveness with which the chemical reaction is accomplished in the combustion chamber. c^* is defined by

$$c^* = \frac{V_j}{C_F} = \frac{g I_s}{C_F} = \frac{gF}{\dot{W}}\left(\frac{1}{C_F}\right) \qquad (3\text{-}20)$$

The experimental determination of c^* can be accomplished by means other than measurement of the thrust developed by the rocket engine. Substituting $F = C_F\, p_c\, A_t$ into equation (3-20), gives

$$c^* = \frac{g}{\dot{W}}\, p_c A_t = \frac{p_c A_t}{\dot{m}} \qquad (3\text{-}21)$$

Thus, the characteristic velocity c^* can be expressed in terms of the parameters I_s, C_F, C_w, W_s as

$$c^* = \frac{V_j}{C_F} = \frac{g I_s}{C_F} = \frac{g}{\dot{W}}\, p_c A_t = \frac{g}{C_w} = \frac{g}{C_F W_s} \qquad (3\text{-}22)$$

3-8. WEIGHTS AND IMPULSE-WEIGHT RATIOS

The take-off weight of a rocket propulsion system, denoted by W_{EO}, is the sum of the weights of the propellants W_p, the complete rocket engine W_E, and the propellant tanks W_T.

If the engine develops a thrust F for the burning time τ_b, then the impulse-weight ratio for the rocket propulsion system, denoted by I/W_{EO}, is given by

$$\frac{I}{W_{EO}} = \frac{1}{W_p + W_E + W_T} \int_o^{\tau_b} F d\tau \qquad (3\text{-}23)$$

If F is constant, then $I = F\tau_b$. The impulse-weight ratio is a criterion of the overall design of the rocket engine, and the largest possible value is desired. For a solid propellant rocket motor, the tank weight $W_T = 0$.

The gross weight or take-off weight of the complete ballistic missile, denoted by W_O, is composed of the weight of the inert metal parts of the missile, denoted by W_M, the weight of the propellants W_p, and the weight of the payload W_U. Thus

$$W_O = W_M + W_p + W_U \qquad (3\text{-}24)$$

The empty weight of the missile, denoted by W_I, is given by

$$W_I = W_M + W_U = W_C + W_E + W_G + W_S + W_U \qquad (3\text{-}25)$$

where W_C = weight of control apparatus
$\qquad W_E$ = dry weight of propulsion engine
$\qquad W_G$ = weight of guidance equipment and its housing
$\qquad W_S$ = weight of structure of the missile
$\qquad W_U$ = weight of payload (the useful load).

For a liquid propellant engine, the engine weight W_E includes the weights of the propellant tanks, gas generator equipment, inert gas storage tanks, the turbopump, plumbing and valves, the control equipment, and the rocket motor assembly. Furthermore, for liquid engines the propellant weight

at take-off W_p includes the weights of all the auxiliary fluids which are required for operating the engine.

In the case of a solid propellant motor, the engine weight W_E includes the weights of the cylindrical casing, the fore and aft caps, the exhaust nozzles, the restriction (inhibiting) liner, the insulation of the fore and aft cap, thrust termination equipment, and of the means for achieving thrust vector control.

The impulse-weight ratio criterion can be also applied to a complete ballistic missile. The magnitude of I/W_O for a given missile depends upon both the specific impulse and density of the propellant combination. If the volume available for the propellants is fixed, it is possible to obtain a larger value for I/W_O from propellants of high density even though they deliver a somewhat smaller specific impulse. It is difficult to generalize regarding the factors influencing I/W_O. Each case should be judged on its own merits.

3-9. MASS RATIOS

Certain mass ratios are useful in analyzing the performances of ballistic missiles.

3-9.1. Propellant Mass Ratio. Consider a rocket jet propelled missile at any instant τ during its powered flight, that is, when $\tau < \tau_b$. For a rocket engine operating under steady conditions the mass rate of propellant consumption $\dot{m}$ is constant. Hence

$$\dot{m} = \dot{W}/g = M_p/\tau_b \qquad (3\text{-}26)$$

The thrust F, also assumed to be constant, is given by

$$F = \dot{m}\ V_j = M_p\ V_j/\tau_b \qquad (3\text{-}27)$$

As the propellants are consumed the total mass of the missile decreases. If M_O denotes the mass of the missile at take-off, then the instantaneous mass of the missile, denoted by m, at any instant during the powered flight ($\tau < \tau_b$) is accordingly

$$m = M_O - \dot{m}\tau = M_O\left(1 - \frac{M_p}{M_O}\frac{\tau}{\tau_b}\right) \qquad (3\text{-}28)$$

At the instant when all of the propellants are consumed, the instantaneous mass of the missile is given by

$$m_b = M_O\left(1 - \frac{M_p}{M_O}\right) \qquad (3\text{-}29)$$

The ratio M_p/M_O is called the propellant mass ratio and is denoted by ξ. Thus

$$\xi = \frac{M_p}{M_O} = \frac{\text{Effective propellant mass}}{\text{Initial mass of vehicle}} \qquad (3\text{-}30)$$

From the point of view of achieving a long range, the propellant mass ratio should be as large as possible.

3-9.2. Vehicle Mass Ratio. The ratio $M_O/(M_O - M_p)$ is called the vehicle mass ratio and is denoted by Λ. Thus

$$\Lambda = \frac{M_O}{m_b} = \frac{\text{Initial mass of vehicle}}{\substack{\text{Mass of vehicle after} \\ \text{consuming propellants}}} \qquad (3\text{-}31)$$

where

$$m_b = M_O - M_p = \text{mass of missile at burnout} \qquad (3\text{-}32)$$

The mass ratios ξ and Λ are related by

$$\xi = 1 - 1/\Lambda \qquad (3\text{-}33)$$

3-10. CUT-OFF OR BURNOUT VELOCITY

A recurring problem in rocketry is the rapid determination of the most suitable rocket jet propulsion system for a given ballistic missile application.

Figure 3-3 illustrates schematically a rocket propelled ballistic missile moving along its trajectory.[1] At any instant $\tau < \tau_b$ the following external forces act upon the missile in the direction of its motion:

   (a) the aerodynamic drag D
   (b) the component of the gravitational force W
        $\sin\gamma = (W_O - \dot{W}_p\tau)\sin\gamma$
   (c) the thrust force F.

The equation of motion (2) for the missile is

$$\frac{W_O - \dot{W}_p\tau}{g}\frac{dV}{d\tau} = F - D - (W_O - \dot{W}_p\tau)\sin\gamma \qquad (3\text{-}34)$$

If A_m is the maximum cross-sectional area of the missile, C_D the drag coefficient, ρ the air density, and V the missile velocity, then the drag D, is given by

$$D = \tfrac{1}{2}\rho\ C_D\ A\ V^2 \qquad (3\text{-}35)$$

[1] A detailed discussion of ballistic missile trajectories is presented in another volume of this series.

If it is assumed that the propellant consumption rate is constant, then the thrust F is given by equation (3-11). Thus

$$F = \dot{m}_p V_j = \frac{\dot{W}_p}{g} V_j$$

Equation (3-34) is a non-linear second order differential equation having non-constant co-efficients. It cannot be integrated directly in closed form but requires a laborious step-by-step process. The quantity generally desired is the velocity of the missile at the instant when burning is completed. That velocity is called either the cut-off, burnout, or burnt velocity.

For preliminary design purposes, optimization studies, and evaluating different engines, an exact solution of equation (3-34) is not needed.

The drag of a rocket propelled missile is proportional to its cross-sectional area A, but its mass is proportional to its volume. For large missiles the effect of aerodynamic drag on the burnt velocity is quite small, about 5 percent for a missile having a take-off weight of approximately 100,000 lb. (6) Consequently, for large missiles the neglect of aerodynamic drag will introduce no serious error especially in view of the assumption that the effective jet velocity remains constant, when actually it increases somewhat with the altitude. For small missiles, on the other hand, the neglect of aerodynamic drag does introduce an error.

3-10.1. Ideal Burnout Velocity. For comparing the performance obtainable from different propulsion engines, a comparison based on assuming no air resistance and no gravitational force leads to a useful criterion; the ideal burnout velocity V_{bi}, also called either the vacuum burnout velocity, or the characteristic velocity.

It can be readily shown that V_{bi} is given by (1, 2, 5)

$$V_{bi} = V_j \log_e \frac{M_O}{m_b} = gI_s \log_e \Lambda \quad (3-36)$$

In terms of the component weights of the missile (see Paragraph 3-8).

$$V_{bi} = gI_s \frac{W_p + W_M + W_U}{W_M + W_U} \quad (3-37)$$

The vehicle mass ratio $\Lambda = M_O/m_b$ is increased by a decrease in the mass of the inert metal parts of the engine.

In the case of booster applications such as JATO or RATO,[1] the payload W_U is very large and the ideal burnout velocity is relatively small, so that a reduction in the metal parts weight of the engine does not give a proportionate increase in V_{bi}. In the case of a ballistic missile, however, the payload W_U is ordinarily only a fraction of the total metal parts weight W_M, and a large value is desired for V_{bi}. For that application the engines must provide a large value for the impulse-weight ratio (I/W_E), and reductions in inert metal parts weight of the engine gives a significant improvement in V_{bi}.

3-10.2. Propellant Weight Loading Density. The ratio of the propellant weight W_p to the engine weight W_E is termed the propellant weight loading density, or engine weight efficiency, (7) and is denoted by δ_p. Thus

$$\delta_p = \frac{W_p}{W_E} = \frac{I/W_E}{I_s} \quad (3-38)$$

It is seen from equation (3-38), that the parameters I/W_E and W_p/W_E are related. Figure 3-4 presents I_s as a function of I/W_E with W_p/W_E as a parameter.

It can be shown (7) that the effect of propellant weight loading density δ_p has a small effect on V_{bi} when the ratio W_E/W_U is small, as in booster applications. On the other hand, in the cases where V_{bi} must be high as for a ballistic missile, a large value for δ_p is essential. (8)

3-11. DRAG-FREE MAXIMUM ALTITUDE

The drag-free maximum altitude is the maximum height obtainable with a vertical trajectory for the case where there is no drag and no initial launching velocity. This quantity obtained by integrating equation (3-34) twice and introducing several simplifying assumptions is discussed in greater detail in another part of this handbook series.

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[1] JATO—Jet Assisted Take-Off employing solid propellant rocket motors. RATO—Rocket Assisted Take-Off employing liquid propellant rocket engines.
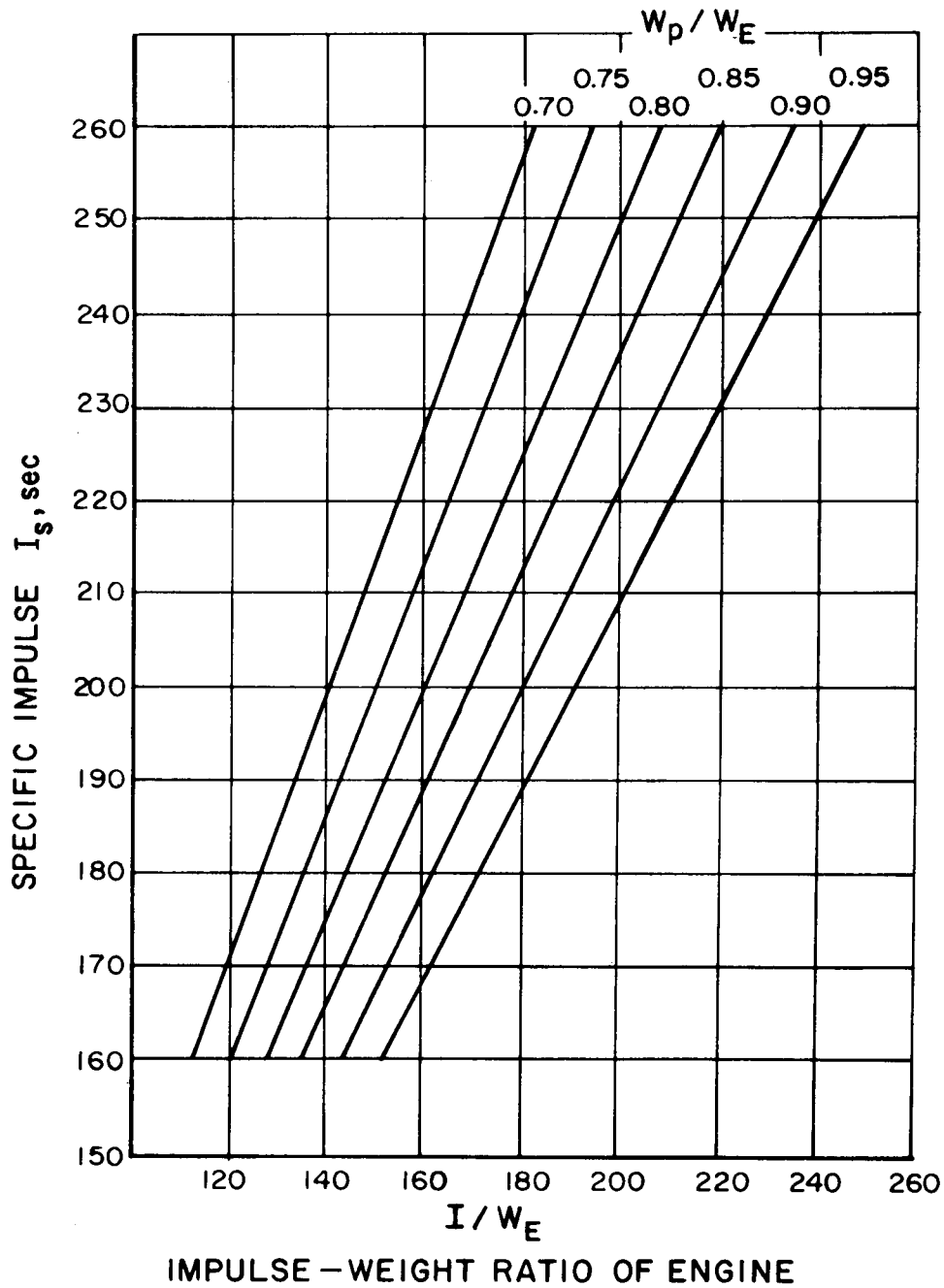
(Taken from Reference 7)

Figure 3-4. Specific Impulse as a Function of the Impulse-Weight Ratio for
Different Values of W_p/W_E

3-12. REFERENCES

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Chapter 4

THERMODYNAMIC RELATIONSHIPS FOR ROCKET ENGINES

4-1. THERMODYNAMIC PROPERTIES REQUIRED FOR CALCULATING THEORETICAL PERFORMANCE CRITERIA

The thrust developed by a rocket engine operating under steady state conditions is practically proportional to V_e, the velocity of the gaseous jet crossing the exit section of the exhaust nozzle (see Paragraph 3-1.3). The kinetic energy of that jet ($V_e^2/2g$), in the case of a chemical rocket engine, is derived from the energy released by the chemical reaction (combustion) of the propellants fed into the combustion chamber. In general, the chemical reaction is exothermic and is accompanied by generation of large quantities of high temperature gases, their pressure being governed by the area of the throat of the exhaust nozzle and the rate at which the propellants are supplied to the rocket engine.

As these gases flow through the exhaust nozzle they are expanded, under substantially adiabatic conditions, so that the gas temperature falls in the direction of flow; that is, the gas temperature at the exit section, denoted by t_e, of the nozzle is lower than it is at the entrance section, denoted by t_c. Since the enthalpy of a homogeneous mixture of gases is a function of the gas temperature, the gases experience an enthalpy decrease in flowing through the exhaust nozzle. The transformation of that enthalpy decrease into kinetic energy of the gaseous jet ($V_e^2/2g$) is given by equation (1-21). The calculation of V_e is, therefore, the first step in computing the desired performance criteria.

4-1.1. Isentropic Exit Velocity and Theoretical Specific Impulse.
In order to compute the performance criteria for a rocket engine from thermodynamic considerations, the following assumptions are introduced: (4)

1. The flow through the nozzle is steady and one-dimensional, and the velocity, V_e, of the gas crossing the exit section (Area A_e) is parallel to the axis of the exhaust nozzle.

2. The velocity of the gases in the combustion chamber is negligibly small compared to the velocity of the gases crossing the exit section of the exhaust nozzle.

3. The flow through the nozzle is isentropic ($dS = 0$).

4. The gases are expanded completely to the surrounding atmospheric pressure p_o; that is, the pressure, p_e, in the exit section of the nozzle is equal to p_o.

5. The gases behave as perfect gases, so that $pv = Rt$.

6. One of the two following assumptions is generally introduced:

   a. The equilibrium composition of the gases in the combustion chamber is unaltered during the expansion process in the nozzle. Calculations employing that assumption are said to be based on frozen equilibrium, or frozen flow.

   b. Chemical equilibrium is maintained throughout the expansion process; the composition and molecular weight of the gas changing because of the chemical reactions occurring during the expansion process. Calculations employing this assumption are said to be based on either equilibrium flow, shifting, mobile, or maintained equilibrium.

Since the flow is assumed to be isentropic, the velocity of the gases crossing the exit section of the exhaust nozzle is denoted by V_e' and called the isentropic exit velocity. If h_c denotes the specific enthalpy of the gases at the entrance to the exhaust nozzle (t_c their corresponding gas temperature is called the combustion temperature), h_e' the specific enthalpy of the gases at the exit section of the exhaust nozzle (t_e' the corresponding gas temperature is called the isentropic exit temperature), p_c the static pressure corresponding to t_c (called the combustion pressure), and p_e the static pressure corresponding to t_e' (called the exit pressure), then V_e' is given by equation (4-1)

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$$V_e' = \sqrt{2gJ(h_c - h_e')} = \sqrt{2gJ \, \bar{c}_p \, t_c Z_t} \quad (4\text{-}1)$$

or

$$V_e' = \sqrt{2g \frac{k}{k-1} R_u \frac{t_c}{\bar{m}} \left[1 - \left(\frac{p_e}{p_c}\right)^{(k-1)/k} \right]} \quad (4\text{-}2)$$

In equation (4-2) the value of k and $\bar{m}$ are suitable average values for the isentropic expansion of the combustion products from the state (t_c, p_c) to (t_e', p_e). It is necessary, therefore, to give careful consideration to the selection of the values for k and $\bar{m}$. The selection of the appropriate value for k is basically the selection of the appropriate value for $\bar{m} \, \bar{C}_p$.

If $\dot{W} = \dot{m}g$ = the propellant weight rate of flow, then the theoretical specific impulse for the propellant combination, denoted by I_s', is given by

$$I_s' = \frac{V_e'}{g} \quad (4\text{-}3)$$

The calculation of the theoretical specific impulse I_s' is basically equivalent to the determination of the isentropic enthalpy change $(h_c - h_e')$. To compute the specific enthalpy h_c the equilibrium composition of the gases produced by the combustion of the propellants and the combustion temperature t_c must be determined. The enthalpy h_e' requires knowledge of the isentropic exit temperature t_e' in the exit section of the exhaust nozzle having the area A_e.

The assumption of frozen equilibrium leads to values of I_s' slightly smaller than those obtained using the assumption of mobile equilibrium (see Paragraph 4-4).

It is apparent from the foregoing that the calculation of the theoretical specific impulse for a propellant system involves determining (a) the combustion temperature t_c, (b) the composition, specific heat ratio k, and molecular weight $\bar{m}$ of the gas, (c) its specific enthalpy h_c, (d) the exit temperature t_e of the gas in the exit plane of the exhaust nozzle, (e) the composition, specific heat ratio, and molecular weight of the gas at the temperature t_e, and (f) its specific enthalpy h_e.

4-2. CALCULATION OF THERMODYNAMIC PROPERTIES OF THE COMBUSTION GAS (1, 2, 3, 4, 10)

It is apparent from the discussions of Paragraph 4-1 that before one can calculate the isen-

tropic exit velocity V_e', and from it the theoretical specific impulse I_s', the thermodynamic properties of the combustion gas at the entrance and exit planes of the exhaust nozzle must be determined. The steps involved in obtaining that thermodynamic data are as follows:

1. The enthalpy of reaction, ΔH_r
2. The combustion temperature, also called the adiabatic flame temperature, t_c
3. The equilibrium composition.

4-2.1. The Enthalpy (or Heat) of Reaction. (4) Consider the general chemical reaction equation

$$a_1 A_1 + a_2 A_2 + \cdots a_n A_n \rightleftharpoons$$
$$b_1 B_1 + b_2 B_2 + \cdots b_m B_m \quad (4\text{-}4)$$
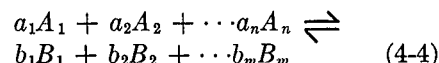
If a_i denotes the number of moles of the i-th species of the reactants, denoted by A_i, and b_j the molar concentration of the j-th species of the products, denoted by B_j, then the above equation can be written in the form

$$\sum_{i=1}^{n} a_i A_i \rightleftharpoons \sum_{j=1}^{m} b_j B_j \quad (4\text{-}5)$$

The enthalpy of reaction, also called the heat of reaction, may be defined as the enthalpy change for a chemical reaction conducted under standard conditions with $\Delta t = \Delta p = 0$. The standard conditions are usually either 298.16°K or 300°K for the temperature and 1 atm for the pressure. Since the combustion of rocket propellants is an exothermic reaction, energy leaves the system wherein the chemical reaction takes place. For that reason the value of ΔH_r for an exothermic reaction is preceded by a negative sign. Since ΔH_r is determined from experiments conducted so that $\Delta t = \Delta p = 0$, the value of ΔH_r depends only on the final and initial states of the chemical species involved. (1) Thus

$$\Delta H_r = \sum (\Delta H_f)_P - \sum (\Delta H_f)_R \quad (4\text{-}6)$$

where $\sum (\Delta H_f)_P$ = sum of the enthalpies of formation for the individual products

$\sum (\Delta H_f)_R$ = sum of the enthalpies of formation for the individual reactants.

The negative of ΔH_r is called the available heat and is denoted by Q_{avail}, thus

$$Q_{avail} = -\Delta H_r \qquad (4\text{-}7)$$

The enthalpy of reaction for an isobaric process ($\Delta p = 0$) is equal to the corresponding change in enthalpy for the system. Thus for the general reaction presented as equation (4-5), it follows that

$$\Delta H_r = \sum_{j=1}^{m} b_j \left[(H_f^o)_{B_j} + \int_{t_o}^{t_c} (c_p)_{B_j} \, dt \right]$$

$$- \sum_{i=1}^{n} \left[a_i (H_f^o)_{A_i} + \int_{t_o}^{t_c} (c_p)_{A_i} \, dt \right] \qquad (4\text{-}8)$$

where t_o is the reference temperature (298.16°K or 300°K), and H_f^o is the enthalpy of formation at the reference temperature (298.16°K or 300°K).

4-2.2. Calculation of Combustion Temperature (Adiabatic Flame Temperature).

The calculation of combustion temperature t_c is based on the following assumptions: (1, 2, 3, 4, 10)

1. The combustion process takes place under adiabatic conditions (no heat is transferred to or from the combustion gas from external sources), consequently the entire enthalpy of reaction ΔH_r for the propellant system is utilized for raising the temperature of the gaseous products produced by the chemical reaction. The combustion temperature t_c is also called the adiabatic flame temperature.
2. The combustion process is isobaric ($\Delta p = 0$).
3. The combustion products are gases and each gas follows the perfect gas equation of state (see Paragraph 1-3.1).
4. Thermodynamic equilibrium is attained by the combustion products (gases) at the entrance to the exhaust nozzle; that is, the free energy change $\Delta \mathcal{J}_{tp} = 0$ (see Paragraph 1-3.8).
5. The velocity of the gases crossing the entrance section of the exhaust nozzle is negligibly small.

Experience has demonstrated that these assumptions do not lead to significant errors in the values for the thermodynamic properties of the combustion products.

Calculation of t_c involves the calculation of (a) the equilibrium composition of the combustion products formed by the reaction of the propellants, and (b) the enthalpy of reaction for the propellant system (the latter is outlined in Paragraph 4-2.1 and the former in Paragraph 4-2.3.).

At the adiabatic flame temperature t_c the combustion gases are in equilibrium and for the present it is assumed that the equilibrium composition is known (see Paragraph 4-2.3). If all of the unreacted reactants are included in the products, then $\sum_{i=1}^{n} a_i$ must vanish, and the heat released by the chemical reaction is utilized for raising the temperature of the products $\sum_{j=1}^{m} b_i B_j$ to the combustion temperature t_c. The temperature t_c is determined from

$$\sum_{j=1}^{m} \left[b_j (H_f^o)_{B_j} \right]_{t_c} - \sum_{i=1}^{n} (a_i)_{t_o} (H_f^o)_{A_i}$$

$$= - \sum_{j=1}^{m} (b_j)_{t_c} \int_{t_o}^{t_c} (C_p)_{B_j} \, dt \qquad (4\text{-}9)$$

where $(a_i)_{t_o}$ represents the initial moles of reactants and $(B_j)_{t_c}$ the moles of products at the temperature t_c.

The equilibrium composition is a function of the combustion temperature and equation (4-9) holds at all pressures for a perfect gas.

The available heat Q_{avail} is given by

$$Q_{avail} = \sum_{j=1}^{m} (b_j)_{t_c} \left[(H_{B_j})_{t_c} - (H_{B_j}^o)_O \right]$$

$$- \left[(H_{B_j})_{t_o} - (H_{B_j}^o)_O \right] \qquad (4\text{-}10)$$

where $(H_{B_j})_{t_c} - (H_{B_j}^o)_O$ represents the enthalpy change per mole of B_j for the temperature change between 0°K and t_c.

Table 2 presents the enthalpies for C-H-N-O compounds as a function of temperature; the reference temperature for the table is $t_o = 298.16°K$.

By applying the principles of the conservation of mass and the equilibrium constants for the reaction (see Paragraph 4-2.3) a set of equations can be obtained for the molar composition of the combustion gas. In general, the equations for the molar balance of each element, together with the equations for the equilibrium constants, give as many equations as there are unknowns so that a

solution can be found for t_c. Only one value of t_c will satisfy equation (4-9) and that value is the adiabatic flame (combustion) temperature.

The procedure for solving the equations for determining t_c is one of successive approximations, and involves the following steps.[1]

1. Assume some reasonable value for t_c and calculate the equilibrium composition of the combustion gas mixture for that temperature (see Paragraph 4-2.3).

2. Using the gas composition calculated under step 1 and equation (4-9), calculate Q_{avail}.

3. Evaluate the right-hand side of equation (4-9) which gives the heat absorbed when the products are heated from t_o to the assumed value for t_c. Denote that result by Q_c.

4. If Q_{avail} from step 2 is larger than Q_c from step 3, then the actual value of t_c is larger than that assumed in step 1;

   If Q_{avail} from step 2 is smaller than Q_c from step 3, then the actual value of t_c is smaller than the chosen value;

   If Q_{avail} from step 2 is equal to Q_c from step 3, then the actual value of t_c is the selected value in step 1.

In practice, sufficient accuracy is obtained by making about three estimates for t_c. For small differences between Q_{avail} and Q_c linear interpolation may be used.

4-2.3. Calculation of Equilibrium Composition.

From equation (4-5) for a general chemical reaction between propellants, it can be shown that when the products may be assumed to be perfect gases, then the summation of the free energies of the products is given by (1) (see Paragraph 1-3.8):

$$\sum_{j=1}^{m} b_j \, \mathcal{J}_{B_j} = R_u t \sum_{j=1}^{m} \ln (B_j)^{b_j} + \sum_{j=1}^{m} b_j \, \mathcal{J}_{B_j}^{o} \quad (4\text{-}11)$$

Similarly for the reactants:

$$\sum_{i=1}^{n} a_i \, \mathcal{J}_{A_i} = R_u t \sum_{i=1}^{n} \ln(A_i)^{a_i} + \sum_{i=1}^{n} a_i \, \mathcal{J}_{A_i}^{o} \quad (4\text{-}12)$$

where $\mathcal{J}_{B_j}$ and $\mathcal{J}_{A_i}$ are the free energies of the species B_j and A_i respectively, $\mathcal{J}_{B_j}^{o}$ and $\mathcal{J}_{A_i}^{o}$ are the

standard free energies of the species B_j and A_i respectively, $(B_j)^{b_j}$ denotes the partial pressure of species B_j raised to its molar concentration b_j, and $(A_i)^{a_i}$ denotes the partial pressure of the species A_i raised to its molar concentration a_i.

For a chemical reaction conducted so that $\Delta t = \Delta p = 0$, which corresponds to the case of measuring the enthalpy of reaction, the free energy change $\Delta \mathcal{J}_{tp}$, is given by (see Paragraph 1-3.8):

$$\Delta \mathcal{J}_{tp} = \sum_{j=1}^{m} b_j \, \mathcal{J}_{B_j} - \sum_{i=1}^{n} b_j \, \mathcal{J}_{A_i} \quad (4\text{-}13)$$

4-2.3.1. Equilibrium Constant.
If $\Delta \mathcal{J}^o$ denotes the standard free energy change for the products and reactants, then

$$\Delta \mathcal{J}^{o} = \sum_{j=1}^{m} b_j \, \mathcal{J}_{B_j}^{o} - \sum_{i=1}^{n} a_i \, \mathcal{J}_{A_i}^{o} \quad (4\text{-}14)$$

Accordingly, the free energy change for the reaction is given by

$$\Delta \mathcal{J}_{tp} - \Delta \mathcal{J}^{o} = R_u t \ln \left[\frac{\displaystyle\prod_{j=1}^{m} (B_j)^{b_j}}{\displaystyle\prod_{i=1}^{n} (A_i)^{a_i}} \right] \quad (4\text{-}15)$$

When the chemical reaction is in equilibrium $\Delta \mathcal{J}_{tp} = 0$. Since $\Delta \mathcal{J}^o$ is a constant, the expression enclosed by the brackets in equation (4-15) is also a constant; the latter is called the equilibrium constant and is denoted by K_p. Thus

$$K_p = \frac{\displaystyle\prod_{j=1}^{m} (B_j)^{b_j}}{\displaystyle\prod_{i=1}^{m} (A_i)^{a_i}} \quad (4\text{-}16)$$

In equation (4-16) the numerator denotes the product of the partial pressures of the individual products raised to the same powers as their molar concentrations. Similarly, the denominator is the product of the partial pressures of each reactant raised to the power of its molar concentration. To illustrate: consider the equilibrium reaction equation

$$H_2O + \frac{1}{2} N_2 \rightleftharpoons NO + H_2$$
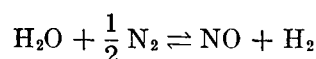
[1] See Example 10.19, Page 536 of Reference 4.

The equation for the equilibrium constant for the latter reaction is accordingly

$$K_p = \frac{(NO)(H_2)}{(H_2O)(N_2)^{1/2}}$$

It follows from the preceding that for a chemical equilibrium reaction involving perfect gases

$$\Delta J^o = -R_u t \ln K_p \qquad (4\text{-}17)$$

The equilibrium constant K_p is a function of the temperature of the gas. Table 4-1 presents the equations for the equilibrium constants for several C-H-N-O compounds. The equilibrium constants for other reactions involving C-H-N-O compounds can be obtained from those listed in Table 4-1. To illustrate:

$$K_{13} = \frac{(O)^2}{(O_2)} = \frac{K_4^2}{K_3}$$

Table 9 presents the equilibrium constants listed in Table 4-1 as functions of the gas temperature. (5, 6)

4-2.3.2. Equilibrium Composition of the Combustion Products.
The method for determining the equilibrium composition of the combustion gas mixture will be illustrated by considering a fuel and oxidizer which produce compounds only of C-H-N-O. Thus

Fuel	Oxidizer

$$(C_w\ H_x\ O_y\ N_z) + (a\ C_{w'}\ H_{x'}\ O_{y'}\ N_{z'}) \qquad (4\text{-}18)$$
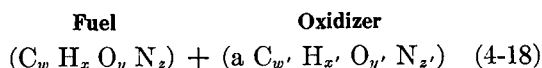
The reaction between the above fuel and oxidizer yields only compounds of the elements C-H-N-O. It will be assumed that the following products are formed: CO, CO_2, H, H_2, H_2O, OH, O, O_2, N, N_2, and NO.[1] At the combustion temperature t_c it is assumed that the products are perfect gases in equilibrium, the corresponding equilibrium equations are presented in Table 4-1 and the equilibrium constants as functions of temperature are presented in Table 9.

For the assumed equilibriums there are seven equations for the pertinent equilibrium constants $K_1, K_2, \ldots K_7$, and eleven gaseous species. For the determination of the moles of CO, CO_2, H, H_2,

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[1] Under certain conditions the combustion products may contain methane, ammonia, and free carbon, and in those cases additional equilibrium equations must be introduced.

H_2O, OH, O, O_2, N, N_2, and NO in the combustion gas mixture, four additional relationships are needed. The latter are provided by the requirement that each of the elements C, H, O, and N must be conserved. Thus

$$\sum C = w + aw' = n_{CO_2} + n_{CO} \qquad (4\text{-}19a)$$

$$\sum H = x + ax' = 2n_{H_2O} + n_{OH} + 2n_{H_2} + n_H \qquad (4\text{-}19b)$$

$$\sum O = y + ay' = 2n_{O_2} + n_O + n_{H_2O} + n_{OH} + n_{NO} + 2n_{CO_2} + n_{CO} \qquad (4\text{-}19c)$$

$$\sum N = z + az' = 2n_{N_2} + n_N + n_{NO} \qquad (4\text{-}19d)$$

where $\sum C$, $\sum H$, etc., represent the total number of gram atoms of carbon, hydrogen, etc.; and n_{H_2O}, n_{OH}, etc., represent the number of gram atoms in the products of the chemical species indicated by the subscripts on the n's.

From equation (1-8) it follows that equations (4-19) can be rewritten in the form of equations relating the partial pressures. Thus

$$(CO_2) + (CO) = \left(R_u \frac{t_c}{v_c}\right) \sum C \qquad (4\text{-}20a)$$

$$2(H_2O) + (OH) + (2H_2) + (H)$$
$$= \left(R_u \frac{t_c}{v_c}\right) \sum H \qquad (4\text{-}20b)$$

$$2(O_2) + (O) + (H_2) + (OH) + (NO)$$
$$+ 2(CO_2) + (CO) = \left(\frac{R_u t_c}{v_c}\right) \sum O \qquad (4\text{-}20c)$$

$$2(N_2) + (N) + (NO) = \left(R_u \frac{t_c}{v_c}\right) \sum N \qquad (4\text{-}20d)$$

where $\sum C$, $\sum H$, etc., denote the total number of carbon atoms, hydrogen atoms, etc., introduced into the reaction, and the parentheses denote the partial pressures of the species enclosed by them.

The last four equations together with the seven equations for the equilibrium constants $K_1, K_2, \ldots K_7$ constitute eleven equations for determining the eleven unknowns CO, CO_2, H, H_2, H_2O, OH, O, O_2, N, N_2, and NO. To solve these eleven simultaneous equations the method generally employed involves the following steps: (4)

1. The partial pressure of each chemical species is expressed in terms of the partial pressure of the pertinent elements and the appropriate equilibrium constants

PROPULSION AND PROPELLANTS

TABLE 4-1. EQUILIBRIUM CONSTANTS FOR C-H-N-O COMPOUNDS

Reaction Equation	Equilibrium Constant
(1) $CO_2 + H_2 \rightleftharpoons CO + H_2O$	$K_1 = \dfrac{(CO)\,(H_2O)}{(CO_2)\,(H_2)}$
(2) $H_2O + \frac{1}{2} N_2 \rightleftharpoons NO + H_2$	$K_2 = \dfrac{(NO)\,(H_2)}{(H_2O)\,(N_2)^{1/2}}$
(3) $2H_2O \rightleftharpoons 2H_2 + O_2$	$K_3 = \dfrac{(H_2)^2\,(O_2)}{(H_2O)^2}$
(4) $H_2O \rightleftharpoons H_2 + O$	$K_4 = \dfrac{(H_2)\,(O)}{(H_2O)}$
(5) $\frac{1}{2} H_2 \rightleftharpoons H$	$K_5 = \dfrac{(H)}{(H_2)^{1/2}}$
(6) $H_2O \rightleftharpoons \frac{1}{2} H_2 + OH$	$K_6 = \dfrac{(H_2)^{1/2}\,(OH)}{(H_2O)}$
(7) $N_2 \rightleftharpoons 2N$	$K_7 = \dfrac{(N)^2}{(N_2)}$
(8) $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	$K_8 = \dfrac{(CH_4)\,(H_2)}{(CO)\,(H_2)^3}$
(9) $\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftharpoons NH_3$	$K_9 = \dfrac{(NH_3)}{(N_2)^{1/2}\,(H_2)^{3/2}}$
(10) $CO + \frac{1}{2} O_2 \rightleftharpoons CO_2$	$K_{10} = \dfrac{(CO_2)}{(CO)\,(O_2)^{1/2}}$
(11) $\frac{1}{2} O_2 + C(graphite) \rightleftharpoons CO$	$K_{11} = \dfrac{(CO)}{(O_2)^{1/2}}$
(12) $\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightleftharpoons NO$	$K_{12} = \dfrac{(NO)}{(N_2)^{1/2}\,(O_2)^{1/2}}$

2. The relationships obtained in Step 1 for the partial pressures of the derived species in terms of the partial pressures of the elements and the appropriate equilibrium constants are introduced into all but one of the conservation of mass equations (4-19)

3. The partial pressures of all of the derived species and all of the elements are then expressed in terms of the partial pressures of a single element and the appropriate equilibrium constants

4. The last expression together with the unused conservation of mass relationship are combined to give an equation in partial pressures of one unknown; the latter is solved by trial and error

5. The result of step 4 is employed for obtaining the partial pressures of all of the constituents and the molar composition of the gas mixture.

From the molar composition of the gas mixture, the specific heats of the individual species, and the

combustion temperature t_c, the enthalpy h_c for the combustion products is readily obtained. Table 2 presents values of enthalpy for C-H-N-O compounds as a function of temperature (see Paragraph 1-3.5).

4-3. THERMODYNAMIC PROPERTIES OF COMBUSTION GAS ASSUMING FROZEN EQUILIBRIUM

The specific impulse calculated upon the basis of frozen equilibrium assumes, in addition to assumptions 1 through 5 of Paragraph 4-1.1, that the average molecular weight $\bar{m}$ of the combustion gas does not change during the expansion process (Assumption 6a, Paragraph 4-1.1). In that case

$$\bar{m} = \sum_{j=1}^{m} (n_j \bar{m}_j)_{t_c} \qquad (4\text{-}21)$$

where n_j represents the mole fraction of the j-th component, and $\bar{m}_j$ its molecular weight, the subscript t_c on the parentheses denotes that the calculation is made for the temperature t_c.

The calculation of the isentropic exit velocity V_e' involves determining the enthalpies h_c and h_e' (see equation 4-1). It has been pointed out that h_c is determined from the composition of the equilibrium gas mixture at the entrance to the exhaust nozzle, and the combustion temperature t_c. The calculation of t_e' for determining h_e' will now be considered.

For an isentropic change of state of 1 mole of a perfect gas

$$\frac{dp}{p} = \frac{k}{k-1} \frac{dt}{t} = \frac{c_p}{R_u} \frac{dt}{t} \qquad (4\text{-}22)$$

Hence, for an expansion from t_c to t_e

$$\int_{p_c}^{p_e} \frac{dp}{p} = \frac{1}{R_u} \int_{t_c}^{t_e'} C_p \frac{dt}{t} = \frac{\bar{C}_p}{R_u} \ln \frac{t_e'}{t_c} \qquad (4\text{-}23)$$

Let $N = \sum_{i=1}^{n} n_i$ = the number of gram moles of gas mixture, then

$$\ln \frac{p_e}{p_c} = \frac{1}{NR_u} \sum_{i=1}^{n} n_i \bar{C}_{pi} \ln \frac{t_e'}{t_c} \qquad (4\text{-}24)$$

In equation (4-24) the nozzle expansion ratio p_e/p_c is specified.

The temperature t_e' is determined from equation (4-24) by trial and error. After the correct value for t_e' has been determined, the correct value for $\bar{C}_p$ is calculated from

$$\bar{C}_p = \sum_{i=1}^{n} \frac{n_i \bar{C}_{pi}}{N} = R_u \frac{\ln p_c - \ln p_e}{\ln t_c - \ln t_e} \qquad (4\text{-}25)$$

The value of k is then calculated from

$$\frac{k}{k-1} = \frac{\bar{C}_p}{R_u} \qquad (4\text{-}26)$$

Neither k nor $\bar{m}$ are sensitive functions of temperature. Consequently, the labor involved in determining the correct value for k and $\bar{m}$ can be reduced without introducing appreciable error by employing the arithmetical mean value for $\bar{C}_p$ for the temperature range t_e' to t_c.

For the gas mixture

$$\frac{p_e}{p_c} = \left(\frac{t_e'}{t_c}\right)^{\Sigma n_i \, C_{pi}/NR_u} = \left(\frac{t_e'}{t_c}\right)^{\bar{C}_p/NR_u} \qquad (4\text{-}27)$$

A trial value of t_e' is calculated from equation (4-27) using the value of $\bar{C}_p$ for the gas mixture at the equilibrium temperature t_c. An arithmetical mean value for the molar specific heat of the gas mixture is calculated from the mean molar specific heats corresponding to the temperature t_c and the trial value of t_e'. This arithmetical mean value of $\bar{C}_p$ is now used in equation (4-27) for obtaining a second trial value for t_e'. The process is repeated until a solution is obtained. The calculation procedure can be reduced by using entropy tables and noting that for the isentropic expansion process in the nozzle, the entropy remains constant.

From the value of t_e' the corresponding value of h_e' can readily be determined from the enthalpy tables for the constituent gases.

For rough approximations it is frequently assumed that the value of k at the combustion temperature t_c does not change during the expansion process.

Values of the theoretical specific impulse I_s' for several liquid propellant combinations based on frozen composition, are presented in Chapter 5.

Table 6 presents the enthalpies of formation of fuels, Table 7 the enthalpies of formation of oxidizers, and Table 8 the enthalpies of formation of reaction products.

4-4. CALCULATION OF SPECIFIC IMPULSE ASSUMING MOBILE (OR SHIFTING) EQUILIBRIUM

In this case assumptions 1 through 5 and assumption 6b of Paragraph 4-1.1 are applicable. The gas composition changes during the isentropic expansion in the nozzle in such a manner that its constituents are always in thermochemical equilibrium. Calculations based on the assumption of mobile equilibrium are concerned with a fixed weight of gas mixture, rather than with a temperature dependent molecular weight of gas.

In general, the values of t_e' and k for mobile equilibrium are somewhat larger than those for frozen equilibrium. Consequently, the corresponding values of V_e' and I_s' are slightly larger.

4-5. CALCULATION OF PERFORMANCE CRITERIA FROM THERMODYNAMIC RELATIONS

Assume that t_c is the equilibrium combustion temperature of the gas mixture at the entrance

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section of the exhaust nozzle, and the value of k is the mean value for an isentropic expansion in the nozzle. Let it further be assumed that the velocity of the gas crossing the entrance section of the exhaust nozzle is negligibly small compared to the isentropic exit velocity V'_e.

If it is desired to take into account the velocity of the gases in the combustion chamber, denoted by V_c, the static values of t_c and p_c are replaced by their corresponding stagnation values T_c and P_c, where

$$T_c = t_c \left(1 + \frac{k-1}{2} M_c^2\right) \qquad (4\text{-}28)$$

and

$$P_c = p_c \left(1 + \frac{k-1}{2} M_c^2\right)^{k/(k-1)} \qquad (4\text{-}29)$$

where $M_c = V_c/a_c$ = Mach number for the gases at the entrance to the exhaust nozzle, and $a_c = (gk R t_c)^{1/2}$ = speed of sound for the combustion gases.

4-5.1. Nozzle Area Ratio for Complete Expansion.
The specific impulse attains its maximum value when the nozzle is designed so that the combustion gases are expanded completely to the predominating back pressure, that is, when $p_e = p_o$. Consequently, the area ratio $\epsilon = A_e/A_t$ for the rocket nozzle is of significance.

$$\epsilon = \frac{A_e}{A_t} = \frac{\left(\dfrac{2}{k+1}\right)^{(k+1)/2(k-1)}}{\left(\dfrac{p_e}{p_c}\right)^{1/k} \dfrac{2}{k-1} \sqrt{Z_t}} \qquad (4\text{-}30)$$

where

$$Z_t = 1 - \left(\frac{p_e}{p_c}\right)^{(k-1)/k} \qquad (4\text{-}31)$$

Figure 4-1 presents the area ratio $\epsilon = A_e/A_t$ as a function of the pressure ratio p_c/p_e.

When $p_e = p_o$ = the atmospheric back pressure, then the gases are expanded completely. The value of A_e/A_t giving complete expansion is called either the optimum area ratio or the area ratio for complete expansion.

4-5.2. Exit Velocity of Gases.
The isentropic exit velocity V'_e for the gases crossing the exit

section of the exhaust, having the cross-sectional area A_e, assuming one-dimensional flow, is given by equations (4-1) and (4-2). The actual exit velocity denoted by V_e is obtained by introducing the velocity coefficient ζ defined by (7).

$$V_e = \zeta V'_e$$
$$= \zeta \sqrt{2g\frac{k}{k-1} R_u \frac{t_c}{m}\left[1 - \left(\frac{p_e}{p_c}\right)^{(k-1)/k}\right]} \qquad (4\text{-}32)$$

The value of ζ is usually between 0.9 and 1.0; its exact value is obtainable only by test. In the absence of test data, the value $\zeta = 0.95$ is recommended for estimating purposes.

It is preferable to estimate $\sqrt{t_c/m}$ from experimental data rather than from thermodynamic calculations.

4-5.3. Weight Rate Flow for Nozzle. (4)
The weight rate of flow of gas through a rocket engine exhaust nozzle is given by

$$\dot{W}' = g\dot{m}' = \frac{A_t p_c \sqrt{gk}}{\sqrt{R_u t_c/m}} \left(\frac{2}{k+1}\right)^{(k+1)/2(k-1)} \quad (4\text{-}33)$$

For convenience let

$$\Omega = \sqrt{k} \left(\frac{2}{k+1}\right)^{(k+1)/2(k-1)} \qquad (4\text{-}34)$$

Then

$$\dot{W}' = g\dot{m}' = \frac{A_t p_c \sqrt{g}}{\sqrt{R_u t_c/m}} \qquad (4\text{-}35)$$

Substituting for g and R_u reduces equation (4-35) to

$$\dot{W}' = g\dot{m}' = 0.1443 \frac{A_t p_c}{\sqrt{t_c/m}} \Omega \qquad (4\text{-}36)$$

Values of the parameter Ω as a function of k are presented in Table 5.

It is seen from equation (4-36) that for a given propellant combination, mixture ratio, and combustion temperature t_c, the rate of propellant consumption $\dot{W}'$ is directly proportional to $A_t p_c$.

For an actual nozzle, the weight flow rate is denoted by $\dot{W}$, where

$$\dot{W} = q\dot{m} = C_d \dot{W}' \qquad (4\text{-}37)$$

(a)

(b)

(c)
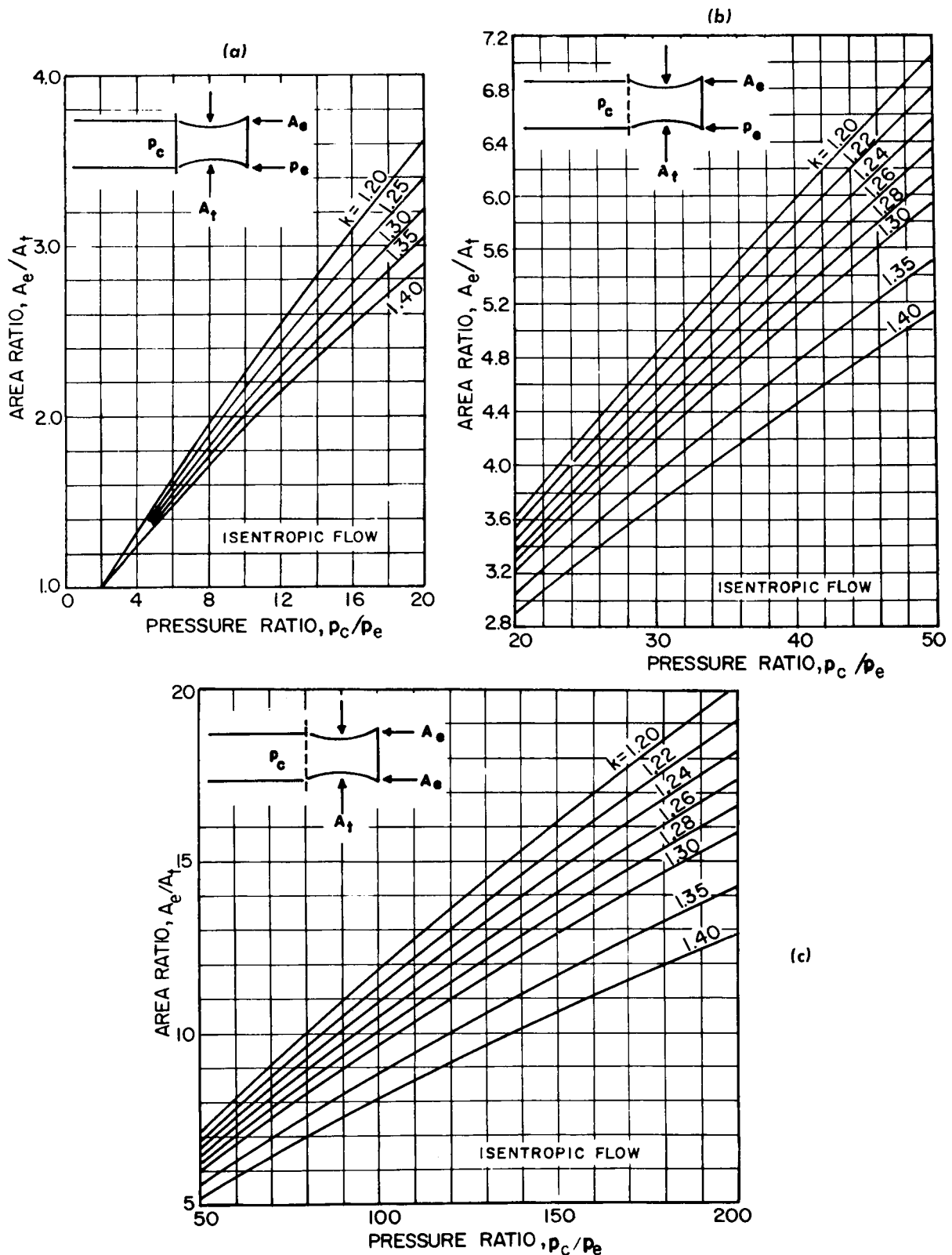
Figure 4-1. Area Ratio of Exhaust Nozzle as a Function of the Pressure Ratio for Different Values of the Specific Heat Ratio

In equation (4-37), $C_d < 1.0$ is the discharge co-efficient for the nozzle.

4-5.4. Calculated Weight Flow Coefficient. The weight flow coefficient is defined by equation (3-17). Hence, the flow, denoted by C'_w, is given by

$$C'_w = 0.1443 \frac{\Omega}{\sqrt{t_c/\bar{m}}} \quad (4\text{-}38)$$

If $C_d < 1$ then the value of C'_w given by equation (4-38) should be multiplied by C_d.

4-5.5. Calculated Thrust Coefficient. The thrust coefficient for a rocket engine is defined by

$$C_F = \frac{F}{p_c A_t}$$

The thrust is given by

$$F = \dot{m} \lambda V_e + (p_e - p_o) A_e$$

where $\dot{m}$ is obtained from equations (4-36) and (4-37). Hence,

$$F = C_d \lambda \zeta V_e \frac{p_c A_t}{\sqrt{g R_u t_c/\bar{m}}} + (p_e - p_o) A_e \quad (4\text{-}39)$$

It is readily shown that (4)

$$C_F = \lambda \zeta C_d \sqrt{\frac{2 k^2}{k-1} \left(\frac{2}{k+1}\right)^{(k+1)/(k-1)} Z_t}$$

$$+ \left(\frac{p_e}{p_c} - \frac{p_o}{p_c}\right) \frac{A_e}{A_t} \quad (4\text{-}40)$$

where Z_t is given by equation (4-31).

It is seen from equation (4-40) that C_F is independent of the combustion temperature t_c and the molecular weight of the combustion gases $\bar{m}$. When the nozzle is designed so that $\epsilon = A_e/A_t$ is the optimum area ratio ($p_e = p_o$), then

$$(C_F)_{optimum} = \lambda \zeta C_d \sqrt{\frac{2 k^2}{k-1} \left(\frac{2}{k+1}\right)^{(k+1)/(k-1)} Z_t} \quad (4\text{-}41)$$

The effect of the atmospheric pressure is to decrease the value of C_F by the amount $(p_o/p_c) A_e/A_t$. If the atmospheric pressure $p_o = 0$ (vacuum), then

$(C_F)_{vacuum}$

$$= \lambda \zeta C_d \sqrt{\frac{2 k^2}{k-1} \left(\frac{2}{k+1}\right)^{(k+1)/(k-1)} Z_t + \frac{p_e}{p_c}} \quad (4\text{-}42)$$

In the ideal case (where $\lambda = 1$, $C_d = 1$, and $\zeta = 1$) the value of C_F is denoted by C'_F; the latter is called the ideal thrust coefficient. The value of C'_F depends on the combustion pressure, the geometry of the exhaust nozzle, and to a minor degree upon the properties of the propellants. (9)

4-5.6. Calculated Specific Impulse. The ideal specific impulse, denoted by I'_s, is given by (see Paragraph 3-2):

$$I'_s = \frac{C'_F}{C'_w} = \frac{V'_e}{g} \quad (4\text{-}43)$$

It follows from equation (4-2), that

$$I'_s = \frac{V'_e}{g} = \frac{1}{g} \sqrt{\frac{2gk}{k-1} \frac{R_u}{\bar{m}} t_c Z_t} \quad (4\text{-}44)$$

If p_o is the static pressure of the atmosphere surrounding the rocket motor, then

$$Z_t = 1 - \left(\frac{p_o}{p_c}\right)^{(k-1)/k} \quad (4\text{-}45)$$

The calculated specific impulse based on one-dimensional flow is denoted by I_s, where

$$I_s = \lambda \zeta I'_s \quad (4\text{-}46)$$

Hence

$$\frac{I_s}{\lambda \zeta \sqrt{t_c/\bar{m}}} = 9.797 \sqrt{\frac{k}{k-1}} \sqrt{1 - \left(\frac{p_o}{p_c}\right)^{(k-1)/k}} \quad (4\text{-}47)$$

The ratio $I_s/\lambda \zeta \sqrt{t_c/\bar{m}}$ is sometimes called the reduced specific impulse. Its magnitude is a function of the specific heat ratio for the combustion gas mixture.

It is seen from equation (4-44) that I'_s depends upon two factors:

(a) $\displaystyle Z_t = \left[1 - \left(\frac{p_e}{p_c}\right)^{(k-1)/k}\right]^{1/2}$

$= $ Expansion Factor (4-48)

and

(b) $\Psi = \left[\dfrac{1}{g} \left(\dfrac{2k}{k-1} \right) \dfrac{R_u\, t_c}{\overline{m}} \right]^{1/2}$

$= $ Flow Factor (4-49)

The magnitude of the expansion factor Z_t depends mainly upon the expansion ratio p_e/p_c and it is only slightly influenced by variations in k. The value of the flow factor Ψ depends primarily upon $\sqrt{t_c/\overline{m}}$. Hence, raising t_c, lowering $\overline{m}$, or doing both, are helpful in increasing the specific impulse.

The combustion temperature t_c is determined by the enthalpy of reaction and the mean specific heat at constant pressure for the combustion gas mixture. A low value for $\overline{C}_p$ is desirable since for the same value of enthalpy of reaction it gives a larger value for t_c. But

$$\overline{C}_p = \overline{C}_v + \frac{R_u}{J} = \frac{R_u}{J} \left(\frac{1}{k-1} + 1 \right)$$

Hence, a low value of $\overline{C}_p$ requires a high value for k, indicating that k is related implicitly to the combustion temperature.

The maximum value of t_c is limited by dissociation reactions. From the point of view of designing a rocket motor, the temperature t_c is also limited by the available materials of construction and the means available for either protecting them from the hot combustion gases or for cooling them. The possibility of increasing the specific impulse by reducing the mean molecular weight of the combustion gas mixture indicates that the fuel should be rich in hydrogen.

4-5.7. Ideal Characteristic Velocity.

The ideal characteristic velocity, denoted by $c^{*\prime}$, (see Paragraph 3-7), assumes that the flow expansion is isentropic. By definition

$$c^{*\prime} = \frac{g\, I_s'}{C_F} = \frac{g}{C_w'} = \sqrt{\frac{g\, R_u\, t_c}{\overline{m}\, k}} \left(\frac{1}{\Omega} \right) \quad (4\text{-}50)$$

where Ω is given by equation (4-34).

Substituting for R_u and g in equation (4-50), yields

$$c^{*\prime} = 223.0\,\Omega \sqrt{\frac{t_c}{\overline{m}\, k}} \quad (4\text{-}51)$$

Equation (4-51) shows that $c^{*\prime}$ depends only upon $\sqrt{t_c/\overline{m}}$ and k; that is, primarily upon the propellant combination and the mixture ratio (oxidizer/fuel by weight). The combustion pressure has only a small effect because it has only a small influence upon the combustion temperature t_c, the molecular weight of the combustion gas mixture $\overline{m}$, and its specific heat ratio k. The preceding remark is particularly true for a composite solid propellant, and is only slightly in error for a liquid propellant system operating under normal conditions ($p_c = 300$ psia or higher). It may, therefore, be assumed without significant error that for given propellants and a fixed mixture ratio (t_c, $\overline{m}$, and k constant) the actual characteristic velocity c^* is independent of the combustion pressure p_c.

From equation (4-51), it follows that

$$\frac{c^{*\prime}}{\sqrt{t_c/\overline{m}\, k}} = \frac{223.0}{\Omega} \quad (4\text{-}52)$$

4-6. REFERENCES

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Chapter 5

PROPERTIES AND CHARACTERISTICS OF LIQUID PROPELLANTS

5-1. FACTORS TO BE CONSIDERED IN SELECTING LIQUID PROPELLANTS

It was pointed out in Chapter 1 that from a broad viewpoint a liquid propellant is any liquid which is injected into the combustion chamber of a rocket engine. By convention, however, the term liquid propellant is applied to any liquid chemical which is an essential component of the chemical reaction for producing high temperature gases in the combustion chamber. Since liquid propellant rocket engines for ballistic missiles utilize bi-propellant systems, the principal interest here is in liquid oxidizers, and liquid fuels.

A great deal of research and development effort has been expended on synthesizing new propellants and improving the properties of the older propellants. As a result there is a large number of liquid propellant systems (oxidizer + fuel) to choose from. However, there is no short-cut method for selecting the most suitable propellant system for a given application. (1) The selection of the most suitable liquid propellants for a given application is greatly influenced by the operating requirements imposed upon the rocket engine. (2) For example, in the case of aircraft applications such as assisted take-off and in-flight-thrust-augmentation, it is usually specified that the performance of the engine be unaffected by change in the operating temperature of the propellants over the range $-65°F$ to $+165°F$. These operating specifications impose stringent limitations upon the number of liquid chemicals that can be considered as propellants for such applications. For certain ballistic missiles, such as the IRBM and ICBM types, the operating temperature specifications can be relaxed materially, thus making certain liquids available that cannot be considered for RATO and IFTA applications.[1] Since there is no propellant which is ideal from all points of view,

one must consider the relative importance of the advantages and disadvantages with respect to the application involved.

From a technical viewpoint alone the selection of a propellant combination (fuel + oxidizer) should be based entirely upon the factors related to obtaining the largest value of impulse-to-weight ratio for the missile. From the standpoints of good engineering and military necessity, the ultimate selection must consider logistics, storage, handling and transport, availability, strategic material requirements and other practical factors. Consequently, the selection of a propellant system involves a compromise between the technical and practical factors pertaining to the application.

Table 5-1 presents the calculated values of specific impulse, based on frozen composition at 500 psia combustion pressure, for several liquid bipropellant systems.

5-2. PRINCIPAL PHYSICAL PROPERTIES

The physical properties which should be considered in selecting a liquid propellant from a performance point of view are discussed in this section. Questions related to the storage and handling of liquid propellants are considered in another volume of this series. Further information on liquid propellants can be found in *Liquid Propellants Handbook*, Battelle Memorial Institute (Confidential), or obtained from Liquid Propellant Information Agency, Applied Physics Laboratory, Johns Hopkins University.

5-2.1. Enthalpy of Combustion. It is desirable that the calorific value per unit weight of a bi-propellant system be as large as possible.

5-2.2. Chemical Reactivity. The bipropellants should react rapidly so that the required residence time for complete combustion is short. Otherwise, large values of the characteristic length L^* will be necessary.

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[1] RATO—rocket assisted take-off with liquid propellant rocket engines. IFTA—in-flight-thrust-augmentation, also called superperformance.

TABLE 5-1. CALCULATED SPECIFIC IMPULSES FOR DIFFERENT LIQUID BIPROPELLANT SYSTEMS

(Conditions: p_c = 500 psia; p_e = p_o = 14.7 psia; isentropic one-dimensional flow; frozen equilibrium during expansion)
r = W_o/W_f = mixture ratio; t_c = adiabatic flame temp.; k = c_p/c_v; $\bar{m}$ = average molecular wt of combustion gases;
ρ = bulk density; I'_s = theoretical specific impulse; I'_d = theoretical density impulse.

Oxidizer	Fuel	r	t_c (°F)	k	$\bar{m}$	ρ (g/cm³)	I'_s	$I'_d = I'_s d$
Bromine pentafluoride	Ammonia	6.0	6660	1.34	29	1.8	235	423
Chlorine trifluoride	Ammonia	3.0	4980	1.32	22	1.26	240	303
	Hydrazine	2.5	6000	1.33	23	1.46	252	368
Fluorine	Ammonia	3.0	7270	1.33	19	1.16	303	351
	Diborane	5.0	7880	1.30	21	1.07	308	330
	Hydrazine	2.0	7740	1.33	19	1.30	316	411
	Hydrogen $(I'_d)_{max}$	19.0	8350	1.34	18	0.75	336	252
	Hydrogen $(I'_s)_{max}$	4.5	5000	1.33	8.9	0.32	373	120
	JP-4	2.9	7100	1.22	24	1.19	278	331
50% Fluorine + 50% Nitrogen trifluoride	Ammonia	2.8	6540	1.32	19	1.15	292	336
Fluorine monoxide	Ammonia	1.9	6040	1.29	18	1.07	280	300
	Hydrazine	1.1	6380	1.28	18	1.23	288	354
	n-Octane	3.8	7340	1.33	20	1.22	301	367
Hydrogen peroxide (99.6%)	Ethyl alcohol (92.5%)	4.0	4600	1.20	23	1.24	240	298
	JP-4	6.5	4830	1.20	22	1.28	248	318
	Hydrazine	1.7	4690	1.22	19	1.24	262	325
Hydrogen peroxide (90%)	Hydrazine	1.5	4170	1.25	18	1.20	252	302
Red fuming nitric acid (6.5% NO₂)	n-Octane	4.5	5100	1.24	24	1.26	234	295
Red fuming nitric acid (15% NO₂)	Hydrazine	1.3	2980	1.25	20	1.26	257	324
Red fuming nitric acid (15% NO₂)	Ammonia	2.15	4220	1.24	21	1.12	236	264
	Diethylenetriamine (80%) + Methylamine (20%)	3.0	5250	1.23	24	1.33	240	319
	JP-4	4.1	5150	1.23	25	1.30	235	305
	Polyethylene	4.5	5320	1.22	25	1.40	233	326
	Turpentine	4.2	5400	1.22	26	1.36	233	316
	UDMH (unsymmetrical dimethyl hydrazine)	3.0	5250	1.23	24	1.33	240	317

If the propellants are hypergolic the engine design is simplified by not requiring an ignition system.

High chemical reactivity is desirable in that there is less danger of explosions from unburned propellants accumulating in the combustion chamber. Furthermore, there is evidence that combustion pressure oscillations are related to chemical reactivity and the susceptibility to them decreases with increased reactivity. (3, 4, 47)

5-2.3. Chemical Structure.[1] The chemical struc-

[1] The derivation of energy from nuclear fission or fusion, the recombination of either ions or free radicals, solar energy and the like is not considered in this volume.

tures of the propellants are important since they determine the composition of the products of their reaction (combustion). It is apparent from equation (4-44) that the specific impulse I_s is practically proportional to $\sqrt{t_c/\bar{m}}$. Reference to Table 5-1 shows that for the liquid propellant systems being considered here, values of I_s as large as approximately 400 seconds are possible in the ideal case. (5) Liquid propellants for high performance rocket engines, such as those for ballistic missiles, must be selected from those liquid chemicals formed from atoms in the first two rows of the periodic table; that is, molecules containing one or more of the following elements C, H, O, N, F, B, and Cl.

TABLE 5-1.—Continued

Oxidizer	Fuel	r	t_c (°F)	k	$\bar{m}$	ρ (g/cm³)	I_s	$I_d=I_s'd$
Nitrogen tetroxide	Hydrazine	1.1	4950	1.26	19	1.20	263	316
Oxides of nitrogen	Ammonia	2.1	4900	1.23	21	1.03	258	267
(70% Nitrogen tetroxide	Ammonia (50%) +							
30% Nitric oxide)	Methyl alcohol (50%)	2.1	5050	1.23	23	1.06	240	255
	Ethylene oxide	2.0	5730	1.24	24	1.14	250	275
	Methyl alcohol	2.1	5210	1.22	25	1.10	236	259
	Turpentine	3.5	5800	1.25	24	1.21	250	303
Oxygen	Ammonia	1.3	4940	1.23	19	0.88	263	231
	Diethylenetriamine	1.5	5550	1.24	21	1.06	266	282
	Ethyl alcohol (75%)	1.3	5150	1.22	23	0.99	246	244
	Ethyl alcohol (92.5%)	1.5	5400	1.21	23	0.98	252	247
	Ethylene diamine (88%)	1.4	6000	1.23	19	1.04	262	272
	Ethylene oxide	1.1	5750	1.24	22	0.99	261	258
	Hydrazine .	0.75	5370	1.25	18	1.06	279	297
	Hydrogen $(I_d)_{max}$	8.0	5870	1.22	16	0.43	316	136
	Hydrogen $(I_s')_{max}$	3.5	4500	1.26	9.0	0.26	363	95
	Isopropyl alcohol	1.7	5560	1.22	22	0.98	258	253
	JP-4 (C/H = 6.85)	2.2	5880	1.24	22	0.98	262	257
	JP-4 (C/H = 6.00)	2.3	5770	1.24	22	0.98	262	257
	Methyl alcohol	1.2	5230	1.21	22	0.95	250	247
	Methyl acetylene	2.0	6180	1.27	22	0.93	241	223
	Methyl cyclopentane	2.3	5770	1.24	22	0.98	263	258
	Nitroethane	0.65	5570	1.23	23	1.09	251	274
	Nitropropane	0.9	5620	1.23	23	1.06	256	271
	n-Octane	2.4	5790	1.23	22	0.96	265	254
	Propylene oxide	1.6	5900	1.23	23	1.00	258	258
	Turpentine	2.4	6000	1.23	22	1.04	261	271
	UDMH	1.4	5650	1.24	20	0.96	272	261
Oxygen (70%) + Ozone (30%)	JP-4	2.3	5950	1.24	22	1.04	268	279
Oxygen (30%) + Ozone (70%)	JP-4	2.3	6180	1.25	21	1.08	272	294
Ozone	JP-4	2.4	6380	1.25	21	1.14	278	317
Tetranitromethane	Hydrazine	1.4	5250	1.27	20	1.29	258	333

Notes:—To obtain values of I_s' and I_d' at combustion pressures other than $p_c = 500$ psia:

p_c	200	300	400	500	600	700	800	900	1000	1100	1200
Multiply by	0.89	0.94	0.98	1.00	1.02	1.03	1.05	1.06	1.07	1.09	1.10

Densities of propellants which boil below 80°F were taken as the values at the boiling point.
Values in table based on "Theoretical Performance of Several Rocket Propellant Combinations," Rocketdyne, a Division of North American Aviation Corporation, Publication 505x, Revised April 1956.

5-2.4. Average Density of Propellant System.

The average density of the propellant system (fuel plus oxidizer), denoted by $\bar{\rho}_p$, should be high so that the dimensions and weights of the propellant tanks, the propellant pressurizing system (see Paragraph 2-4.2), and the associated plumbing are minimized. In general, liquid fuels have smaller densities than liquid oxidizers so those propellant systems giving satisfactory values of specific impulse with large values of mixture ratio r (where $r = \dot{W}_o/\dot{W}_f$) yield large values of average propellant density $\bar{\rho}_p$, and in most cases large values of density impulse I_d.

The density of a liquid propellant system is a function of its temperature. In the case of a petroleum fuel, such as JP-4 or JP-5, the density also varies with its chemical composition. Ordinarily, it is desirable to maintain a constant mixture ratio r for the propellants burned during the powered flight of the missile, so that both fuel and oxidizer tanks will be emptied practically simultaneously. To achieve that objective some form of automatic propellant utilization system must be provided to maintain r at the requisite value.

In the case of a long range ballistic missile the variations in propellant density due to aerodynamic heating are generally quite small because the missile is beyond the dense atmosphere surrounding the earth in less than one minute of the powered flight. (4)

5-2.5. Boiling Point and Vapor Pressure. A high boiling point, preferably above 160°F, is desirable so the propellant can be stored in light weight tanks and without excessive loss by evaporation. Preferably the vapor pressure should be small at temperatures up to approximately 160°F. Otherwise, the evaporation of the propellant in storage will be excessive and vacuum jacketed tanks may be required.

The boiling point and vapor pressure characteristics of a propellant exert a major influence upon the design and operating characteristics of the pressurizing system, particularly in the case of a turbopump system (see Paragraph 2-4.2). Because of their low weight, high speed centrifugal pumps are employed exclusively in the turbopumps of large liquid propellant ballistic missiles. Propellants having low boiling points and high vapor pressures tend to induce cavitation phenomena in the pumps and supply lines. To prevent the occurrence of cavitation and vapor lock problems the propellant tanks have to be pressurized with an inert gas, usually nitrogen or helium, so that pressures at all points in the feed system are above that inducing cavitation. (6) Propellants having large vapor pressures increase the required gas pressures and may necessitate increasing the thickness, and consequently the weights, of the propellant tanks.

5-2.6. Freezing Point. It is desirable that the propellant remain liquid at the lowest temperature to be encountered in storage on the ground and in flight. For certain applications some liquid chemicals cannot be considered for use as rocket propellants if their freezing points are above −65°F.

5-2.7. Viscosity. It is desirable that the viscosity of a liquid propellant be low at all operating temperatures; preferably less than 10 centipoises at −65°F. Otherwise, the pressure drop required for transferring the propellant from the supply tank and injecting it into the rocket engine becomes excessive.

5-2.8. Specific Heat. If the propellant is utilized for cooling the rocket engine by forced convection, as in a regeneratively cooled rocket engine (see Paragraph 2-4.1), a high specific heat is advantageous. The total heat a regenerative coolant can absorb is equal to the product of its flow rate, specific heat, and temperature rise between its inlet and saturation temperatures. From a cooling standpoint a high saturation temperature is also desirable. The saturation temperature should be at least 300°F but should not exceed approximately 700°F if the wall temperatures are to be kept from becoming dangerously high. (7)

5-2.9. Chemical Stability. The propellant should be stable chemically when stored within the desired temperature range for reasonable times. It must also be stable at the temperatures it will encounter in the operation of the rocket engine. In that connection liquid chemicals which decompose and deposit salts when utilized as a regenerative coolant may not be usable for certain applications. (2)

It is preferable that the liquid propellant shall not decompose violently when heated, nor should it be sensitive to shock.

5-2.10. Corrosivity. It is desirable that the propellant have a low chemical activity with the materials used for storage containers, valves, piping, rocket motors, bearings, pumps, gaskets, etc. Otherwise, problems arise concerned with the storage and handling of the propellant, and the design of engine components.

Ordinarily, the fuel component of a bipropellant combination introduces fewer material selection problems than the oxidizer. Nevertheless, the compatibility of the fuel with available construction materials should be considered, since several of the possible fuels do attack the more common metals and plastics.

The selection of the most appropriate materials for all of the components of a liquid propellant rocket engine is one of the major problems entering into the design and construction of a satisfactory engine.

5-2.11. Toxicity. It is desirable that the toxicity of the liquid propellant be low so that it can be handled with conventional equipment and procedures. (11, 12, 24)

5-2.12. Availability. Rocket propellants which would be used in large quantities during an emergency, must either be readily available or their production potential must be ample to meet the anticipated demand.

5-2.13. Cost. In evaluating the cost of propellants for a ballistic missile, the total amount of propellants supplied to the missile from the time it is placed in service readiness to the completion of its firing must be taken into account. It is the total impulse of the missile divided by the cost of all of the propellant consumed that determines the impulse per unit of cost. Of course, a large value of impulse per unit of cost is desirable.

5-3. MONOPROPELLANTS

Since the beginning of World War II a large number of monopropellants have been investigated in this and other countries. The principal systems are listed below:

1. mixtures of methyl nitrate and methanol (myrols)
2. mixtures of nitrobenzene, nitric acid and water (dithekites)
3. mixtures of nitroparaffins
4. ethylene oxide
5. concentrated hydrogen peroxide (HTP)
6. hydrazine

As pointed out in Paragraph 2-3.1, monopropellants appear to combine energy content with high shock sensitivity and their performances are too low for them to be useful as the main propellant for a rocket engine propelling a ballistic missile. Of the aforementioned monopropellants only hydrogen peroxide and hydrazine find wide use as the oxidizer and fuel component respectively of bipropellant systems. They also are used extensively for generating high temperature gases for driving either the turbine of the turbopump for the rocket engine or that of the auxiliary power unit (APU) where one is employed in the missile. For the purpose of completeness brief comments will be made regarding monopropellants 1 to 4 inclusive, and more detailed discussions will be presented on hydrogen peroxide and hydrazine.

5-3.1. Mixtures of Methyl Nitrate and Methanol (Myrols). The Germans investigated these mixtures extensively, and concluded that the specific impulses were too low (of the order of 180 sec) and that they were too sensitive to shock. It is worth noting that methyl nitrate is almost as shock sensitive as nitroglycerine.

5-3.2. Nitrobenzene—Nitric Acid—Water Mixtures (Dithekites). These monopropellants were investigated by the Germans, who found that unless the mixture contained at least 20 percent water by weight it was too sensitive for use as a monopropellant. The specific impulses obtainable with dithekites ranged from 190 to 208 sec.

5-3.3. Mixtures of Nitroparaffins. After a rather extensive investigation, nitromethane, one of the few monopropellants giving a reasonable specific impulse (220 seconds at 300 psia), was abandoned as a rocket propellant primarily because of its shock sensitivity and the problem of obtaining efficient combustion in a motor having a reasonable characteristic length L^*. Studies of mixtures of nitromethane with nitropropane to reduce shock sensitivity, showed that as the shock sensitivity of the mixture was decreased through increasing the percentage of nitropropane, the specific impulse decreased to unacceptable values.

5-3.4. Ethylene Oxide. Because of the safety with which it can be handled, ethylene oxide (C_2H_4O) has received extensive study during the past decade. This material decomposes into carbon monoxide (CO) and methane (CH_4).

Because it has a low flash point it must be handled as carefully as gasoline. Although it is insensitive to shock it will ignite if in contact with catalytic surfaces. It can be stored in steel or stainless steel drums and is readily available commercially. (8, 9)

Ethylene oxide has been used as the source of high temperature gases for driving the turbines of auxiliary power units (APU).

5-3.5. Hydrogen Peroxide. Hydrogen peroxide is used as a rocket propellant in concentrations ranging from 80 to 95 percent. Its first use was by the Germans (concentration approximately 80 percent) in 1933. (10) Table 5-2 presents the physical properties of hydrogen peroxide solutions as a function of their concentration. (12, 13, 14, 15, 16)

TABLE 5-2. PHYSICAL PROPERTIES OF DIFFERENT CONCENTRATIONS OF HYDROGEN PEROXIDE IN WATER

Concentration, percent	100	90	80
Specific heat, Btu/lb°F at 64.4°F	0.57	0.61	0.65
Freezing point, °F	30.4	12.6	−10.8
Boiling point, °F	312	288	269
Specific gravity at 64.4°F	1.450	1.394	1.341
Viscosity, centipoise at 64.4°F	1.307	1.301	1.297
Heat of vaporization, Btu/lb	540	588	634
Vapor pressure, psi at 100°F	0.007	0.012	0.016

Hydrogen peroxide can be readily decomposed thermally with suitable catalysts according to the equation

$$H_2O_2(liq) = H_2O\ (g) + \tfrac{1}{2}\ O_2\ (g) + 23,300\ Btu$$
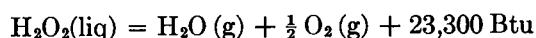
According to thermochemical calculations based on the above equation, when 100 percent H_2O_2 used as a monopropellant is decomposed at a pressure of 300 psia, the temperature of the decomposition gases (H_2O and O_2) is 1800°F, and the theoretical specific impulse obtained by expanding those gases to standard sea level is 146 sec.

The kinetics of the catalytic decomposition of hydrogen peroxide solutions has been studied extensively in this and other countries. Sodium and calcium permanganate solutions are effective catalysts for decomposing hydrogen peroxide. As a matter of fact the Germans developed propulsion systems based on injecting a small quantity of a solution of either sodium or calcium permanganate into the rocket engine simultaneously with the hydrogen peroxide solution. (10) Calcium permanganate was preferred because of its much greater solubility in water. Once the decomposition of the peroxide has been initiated it proceeds smoothly. The decomposition equation is

$$H_2O_2 + Ca\,(MnO_4)_2 = Ca(OH)_2 + 2\,MnO_2 + 2\,O_2$$

Calcium permanganate can also be used as a catalytic surface. Alundum pellets are soaked in a strong solution of calcium permanganate for several hours, dried, and packed into a chamber called the decomposition chamber. The concentrated hydrogen peroxide decomposes in flowing through the bed of pellets. In this country, the trend in recent years is to use silver surfaces as the decomposition catalyst. Silver screens are placed in the decomposition chamber, thereby exposing a large surface to the hydrogen peroxide and its vapors.

Concentrated hydrogen peroxide as a rocket propellant suffers from the following disadvantages: it is thermally sensitive, chemically unstable, and has a relatively high freezing point.

Because of the interest in concentrated hydrogen peroxide solutions, particularly by the British and Germans (16, 18, 19), the problems of handling and storing such solutions have been thoroughly investigated. Experience has demonstrated that the pure material can be stored for reasonable periods of time in vented containers made from specially treated aluminum. The aluminum content of the container material should not be less than 99.7 percent and its copper content not greater than 0.06 percent. A great deal of research effort has been devoted to improving the storability characteristics of concentrated hydrogen peroxide, but despite all the progress which has been made it must still be stored in vented containers. Great care must be exercised to avoid introducing into the storage containers impurities such as iron oxide (rust), organic matter, dust, copper, and other materials which catalyze the decomposition of hydrogen peroxide. (13, 14, 18)

It is found that oxygen gas is continuously evolved from concentrated hydrogen peroxide solutions, even at ambient temperatures, but at low temperatures the rate of gas evolution is low enough to be considered negligible.

The relatively high freezing points of concentrated hydrogen peroxide solutions (see Table 5-2) are disadvantageous for many applications. Considerable research has been expended on investigating materials for depressing the freezing points of concentrated hydrogen peroxide solutions. The three which have been investigated most thoroughly are water, ammonium nitrate, and glycols.

Much effort has also been expended on investigating the ternary system hydrogen peroxide-ethylene glycol-water. To obtain a low freezing point with the latter mixture the water content must be relatively large (more than 20 percent by weight). This reduces the oxygen content of the mixture, and makes the latter unsuitable for application as the oxidizer in a bipropellant system. It does, however, have application as a

monopropellant; the ethylene glycol increases its energy content. (15)

5-3.6. Hydrazine.

Hydrazine (N_2H_4) is a toxic colorless liquid having the following physical characteristics: specific gravity 1.01, freezing point 34°F, and boiling point 236°F. Hydrazine can be used as the fuel component in a liquid bipropellant system or as a monopropellant. It is readily soluble in water, alcohol, and certain organic liquids. The water solution, hydrazine hydrate ($N_2H_4 \cdot H_2O$), was used as the fuel with concentrated hydrogen peroxide as the oxidizer for the Walter power plant to propel the ME 163 airplane. Hydrazine and its hydrates are toxic and exposure to their vapors may cause temporary blindness. (21, 22, 23)

Because it is thermally unstable, hydrazine can be caused to undergo an exothermic decomposition, which apparently takes place in two steps (11, 12, 23) as follows:

(a) $\quad 3\,N_2H_4 = 4\,NH_3 + N_2 \quad + 144{,}300\,\text{Btu}$

(b) $\quad 4\,NH_3 = 2\,N_2 + 6\,H_2 \quad - 79{,}200\,\text{Btu}$
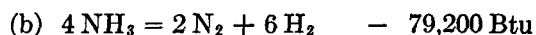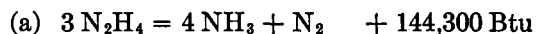
It is seen from the above that the specific impulse obtained from the thermal decomposition of hydrazine will depend upon which reaction products are formed. Because the decomposition of the ammonia (by reaction b) is endothermic, decomposition according to reaction (a) gives the higher specific impulse. Reaction (b), the decomposition of ammonia (NH_3), is generally a slow process, so if the reaction time is limited as is usually the case, only a small portion of the ammonia formed by reaction (a) will become dissociated. Hence, the decomposition of hydrazine gives a larger specific impulse if the characteristic length L^*, which is a measure of the time available for decomposing the hydrazine, is short enough to prevent any substantial decomposition of the ammonia formed by reaction (a).

Experiments, principally by Jet Propulsion Laboratory, California Institute of Technology (JPL/CIT), have demonstrated that the decomposition reaction for hydrazine is influenced by temperature and the presence of catalysts. Accordingly it is difficult to specify the exact stoichiometry in a given case. Hence, if x denotes the fraction of the ammonia which is decomposed, reactions (a) and (b) can be combined to give (23)

(c) $\quad 3\,N_2H_4 = 4(1-x)\,NH_3 + (1+2x)\,NH_3$
$\quad + 6\,x H_2 + (144{,}300 - 79{,}200x)\text{Btu}$
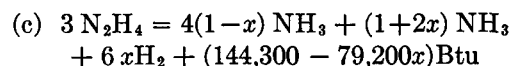
If the performance parameters for hydrazine are plotted as a function of the percent of ammonia dissociated, it is found that when $x = 0$, $I_s = 192$ sec and when $x = 100$, $I_s = 168$ sec.

The following materials catalyze the decomposition of hydrazine: metallic iron, nickel, and cobalt supported on porous aluminum oxide. By employing a catalyst the primary decomposition reaction can be accelerated. Furthermore, it is possible to control the decomposition of the hydrazine so that gases having different molecular weights and temperatures are obtained. Consequently, by proper control of the decomposition reactions, gases can be generated which are suitable for operating either gas turbines or for pressurizing propellant tanks.

Such gases have the advantage that they contain no solids or condensable constituents.

The principal disadvantage encountered in the application of hydrazine is its high freezing point (34°F). Experiments have shown that the freezing point can be depressed by adding nitric acid (HNO_3) and water to the hydrazine. Solutions containing more than 17 percent nitric acid by weight tend to become unstable and shock sensitive. A rather thorough investigation has been conducted at JPL/CIT for a mixture consisting of 74 percent N_2H_4, 16 percent HNO_3, and approximately 10 percent water by weight. This mixture has a freezing point of approximately −40°F, and can be decomposed to give gases having a temperature of approximately 1700°F. The loss in performance in a gas turbine operated on those gases instead of the decomposition products of pure hydrazine, is approximately 5 percent. Because the decomposition products of the mixture contain approximately 20 percent water they are not suitable for pressurizing propellant tanks. (22)

Experiments indicate that the mixture can be handled in much the same manner as pure hydrazine, and that it can be stored for long periods of time at ambient temperatures in unvented aluminum or stainless steel containers, without serious decomposition.

5-4. OXIDIZERS FOR LIQUID BIPROPELLANT SYSTEMS

The performance of a bipropellant system depends upon the thermodynamic properties of the oxidizer and of the fuel. Reference to Table 5-1, which presents "Calculated Specific Impulses for Different Liquid Propellants," shows that the characteristics of the oxidizer have a greater effect upon the specific impulse than do those of the fuel. It was pointed out in Paragraph 2-3.2 that only a few liquid materials can be used as practical oxidizers. For that reason, when selecting a bipropellant system for a given application, the usual procedure is first to select the oxidizer and then that fuel which when used with the oxidizer gives the most favorable bipropellant system from all points of view (see Paragraph 5-1).

The atoms that are useful as oxidizers in rocket propellant systems are oxygen and fluorine since they give highly exothermic combustion reactions. Consequently, the suitable liquid oxidizers are either the elements oxygen and fluorine or compounds containing a large proportion of those elements. (11, 23) For a material to be a suitable oxidizer it should not have a large enthalpy of formation, otherwise its enthalpy of combustion will be relatively small. (48) A low enthalpy of formation indicates low bond energies between the atoms in the molecule.[1] The requirement of low bond energies suggests that the most suitable compounds are those containing the nonmetallic elements (Groups V, VI, and VII of the periodic table). The single exception is hydrogen, which occurs in many oxygenated compounds. The large bond energy of hydrogen (103.4 kcal/mol) causes a loss in combustion energy, but the low atomic weight of hydrogen partially compensates for that loss. For these reasons the liquid oxidizers which are useful in rocketry are primarily compounds containing the elements fluorine, hydrogen, nitrogen, and oxygen. The prime oxidizers are, of course, fluorine and oxygen. Table 5-3 presents the physical properties of the more important oxidizers.

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[1] Bond energy may be defined as the average energy per mole which must be absorbed to break a particular bond in a molecule and separate the resulting atoms or radicals from each other.

5-4.1. Liquid Fluorine.
A given fuel yields a larger enthalpy of reaction with liquid fluorine than with liquid oxygen because the hydrogen in the fuel forms HF which has greater stability than the H_2O formed with oxygen. Because fluorine is monovalent while oxygen is divalent, more fluorine than oxygen is required for burning a given fuel. Since the specific gravities of oxidizers are, in general, larger than those of fuels, the larger mixture ratios required with fluorine oxidizers result in the propellant system (fuel plus oxidizer) having a higher average density. To illustrate, consider the combustion of anhydrous liquid ammonia (NH_3) in stoichiometric proportions with fluorine and with oxygen. The specific impulse obtained from the F_2-NH_3 system is 313 sec and its average specific gravity is 1.20. For the O_2-NH_3 system the corresponding values are 255 sec and 0.89. Figure 5-1 is a bar-graph chart which compares the performances of several fuels when burned with either liquid fluorine or liquid oxygen, at 500 psia combustion pressure. (24, 25) It is seen that the largest value of specific impulse is obtained with the fluorine-hydrogen system (373 sec at 500 psia). The corresponding flame temperature is 7940°F and the molecular weight of the jet gases is 8.9.

It must be borne in mind that from the standpoint of rocket engine performance fluorine burns efficiently only with hydrogen. A series of fluorocarbons is formed when fluorine is burned with carbon, e.g., CF, CF_2, CF_3, and CF_4. Consequently, if a fuel contains both hydrogen and carbon atoms, the best performance with that fuel is obtained with an oxidizer containing both fluorine and oxygen, so that the hydrogen is burned with the fluorine and the carbon with the oxygen.

Although liquid fluorine is the best oxidizer from the point of view of obtaining high specific impulse and a large average density, it has several disadvantages, the three principal ones being its low boiling point (−188°C), its extreme chemical activity, and its high toxicity. Compared to liquid oxygen it is much more expensive, less available, and more hazardous to handle. The logical application for liquid fluorine is for long-range missiles where its superior performance can be utilized advantageously.

Fluorine reacts readily with most metals, organic matter, concrete, glass, and water. Once the

TABLE 5-3. PHYSICAL PROPERTIES OF LIQUID OXIDIZERS

(Based on Reference 23)

Oxidizer	Av. Molecular Weight $\overline{m}$	Density ρ (g/cc)	Melting Point °C	Boiling Point °C	Heat of Vaporization Q_v (kcal/mol)	Heat of Formation Q_f (kcal/mol)	Specific Heat C_p (cal/C/mol)	Viscosity μ (centipoise)
A. OXIDIZERS CONTAINING FLUORINE								
F_2	38	1.55^{-187}	-217.9	-188	1.51	3.0^{-188}	11.3^{-188}	0.28^{-193}
ClF_3	92.5	1.77^{12}	-82.6	12.1	5.74	42.7^{25}	28^{25}	0.48^{25}
BrF_3	175	2.47^{25}	-61	40.5	—	—	—	—
BrF_5	137	2.84^{9}	8.8	127	10	—	—	—
IF_5	222	3.5	-8	97	—	—	—	—
IF_7	260	2.8	5.5	4.5	—	—	—	—
NF_3	71	1.54^{-129}	-209	-129	2.77	31.2^{-129}	—	—
B. OXIDIZERS CONTAINING OXYGEN								
O_2	32	1.14^{-183}	-218.4	-183	1.63	3.09^{-190}	13.0^{-183}	0.19^{-183}
O_3	48	1.71^{-111}	-251.4	-111.5	2.59 3.65^{-183}	-30.3^{-110}	17^{-112}	1.56^{-183}
H_2O_2	34	1.44^{20}	-0.9	150.5	11.1	44.8^{25}	19.7^{20}	1.83^{0}
HNO_3	63	1.51^{20}	-41.6	86	9.43	41.4^{25}	26.3^{20}	0.91^{20}
MON*	92	1.45^{20}	-11.3	21.0	9.1	6.8^{25}	33^{20}	0.43^{20}
N_2O	44	1.23^{-89}	-102.4	-88.5	3.96	-19.5	18.6^{-88}	—
NO	30	1.27^{-151}	-163.6	-151.8	3.29	-21.6	18.7^{-151}	—
$C(NO_2)_4$	196	1.65^{13}	13	125.7	—	$-(22)$	—	—
SFNA**	62.7	1.56^{20}	-54	60	9.4	41.1^{25}	26.7^{20}	1.37^{20}
F_2O	54	1.53^{-145}	-223.8	-144.8	—	-1.4^{-188}	11.3^{-188}	—
70% F_2 + 30% O_2	—	1.45^{-187}	-218	-186	—	—	—	—
ClO_3F	102.5	1.43^{68}	-145	-56	—	7.3^{25}	26.7^{20}	0.18^{20}

Notes:—Superscript denotes temperature of measurement in °C.

* MON—mixed oxides of nitrogen (equilibrium mixture of NO_2 and N_2O_4).

** SFNA—stabilized fuming nitric acid (83.5% HNO_3, 14% NO_2, 2% H_2O, 0.5% HF).

RFNA—red fuming nitric acid (84% HNO_3, 14% NO_2, 2% H_2O).

reaction has started it cannot be stopped because the fluorine reacts with water. It can be stored, however, at temperatures below 100°C, in clean dry containers made from copper, nickel, monel metal, and aluminum. This is because a protective film of metal fluoride is formed that adheres tenaciously to the metal surface.

Because of the difficulties in handling liquid fluorine and its low availability, it appears that for the next few years at least, liquid fluorine will be considered only for special strategic missiles.

In general, all oxidizers containing fluorine produce large quantities of HF in the exhaust gases discharged from the rocket engines using them. Undoubtedly this has been a deterrent to the development of fluorine or fluorine-containing oxidizers. Recent experiments have demonstrated that there is insignificant contamination and corrosion of the firing site associated with burning fluorine in rocket engines of moderate size. Because of its low molecular weight the HF tends to dissipate rapidly in the air.

5-4.2. Liquid Oxygen (LOX). Historically, LOX was one of the first oxidizers used in liquid propellant rocket systems. Currently, it is the oxidizer used in such ballistic missiles as the Atlas, Titan, Jupiter, Thor, and Redstone. Excepting the fluorine group of oxidizers and ozone, LOX gives the best performance, on a weight basis, of any oxidizer. Since it is prepared from liquid air by fractional distillation, it can be produced cheaply

PROPULSION AND PROPELLANTS

SPECIFIC IMPULSE VALUES AT 500 psia
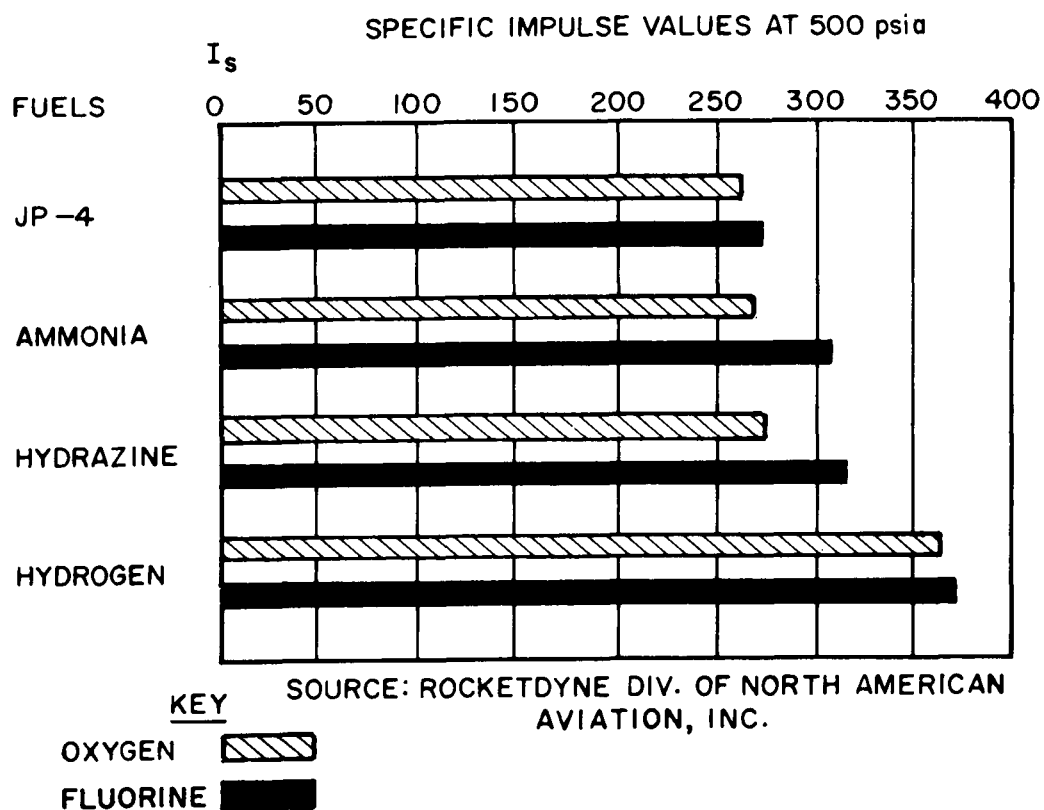
Figure 5-1. *Performance of Several Fuels with Fluorine and with Oxygen*

(about 3 cents per lb) at any desired site, and because of its widespread industrial use the manufacturing and handling technology is well developed. Recent years also have brought the development of air transportable LOX generators.

The principal disadvantages of LOX arise from its being a liquefied gas, and the fire risk attendant to its use. Because of its volatility its transport and storage introduce severe problems. If stored in bulk in insulated tanks the loss due to evaporation is of the order of 3 percent per day, but stored in vacuum jacketed tanks the evaporation loss can be reduced to a fraction of a percent per day. It does not appear feasible at this time either to transport or store LOX in the oxidizer tanks of missiles, so the missiles must be loaded with LOX in the field or at the launching site. Consequently, LOX generators must be provided to replace the losses of LOX due to evaporation.

Even though a relatively small quantity of LOX is actually consumed in firing a missile, its real cost is much greater than might be assumed from the fact that it is plentiful and can be produced cheaply. The cost of storage tanks, LOX generators, evaporation losses, and the maintenance of an extensive personnel to service LOX missiles must be included in the actual cost of LOX used.[1] Thus, despite its plentiful supply, low cost of production, and broad background of industrial and military use, LOX is really unsuitable as the oxidizer for tactical missiles. In fact, when all the problems and costs concerned with handling, storaging, servicing, complexity, and cost of LOX missiles are considered, it appears probable that LOX may not even be the best choice of oxidizer for some of the missiles in which it is currently being used.

5-4.3. Oxidizers Containing Fluorine. The compounds of fluorine with the nonmetallic elements nitrogen, chlorine, bromine, and iodine are of interest because the fluorine atoms are relatively loosely held in those compounds. The properties of several fluorine compounds are presented in Table 5-3.

Of the compounds listed in Table 5-3, only ClF_3 and NF_3 contain a large enough percentage by weight of fluorine to give good performance.

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[1] The statements are to a large degree applicable to all cryogenic propellants.

Bromine pentafluoride (BrF_5) may be of interest because of its high specific gravity.

5-4.3.1. Chlorine Trifluoride (ClF_3). Although nitrogen trifluoride (NF_3) gives higher performance than chlorine trifluoride (ClF_3) it has not received as much attention as ClF_3, because NF_3 is a liquefied gas at ambient temperatures (see Table 5-3). Chlorine trifluoride has a large specific gravity (1.82), a low freezing point ($-83°F$), and can be handled as a liquid at ambient conditions; its vapor pressure is less than 100 psia at 160°F. Reference to Table 5-1 shows that when reacted with hydrazine (N_2H_4) and ammonia (NH_3) at 500 psia, the corresponding values of specific impulse based on frozen composition, are 240 sec and 252 sec respectively.

Since ClF_3 is produced by the direct reaction between gaseous chlorine and gaseous fluorine its availability depends upon the potential supply of fluorine.

The exhaust products of a rocket motor burning ClF_3 contain both hydrogen fluoride (HF) and hydrogen chloride (HCl). The higher molecular weight of the latter can cause it to persist in the launching area especially on a humid day (see Paragraph 5-4.1).

5-4.4. Oxidizers Containing Oxygen. The principal oxidizers containing oxygen atoms and no fluorine atoms are liquid ozone (O_3), hydrogen peroxide (H_2O_2), nitric acid (HNO_3), and mixtures of nitrogen dioxide (NO_2) with nitrogen tetroxide (N_2O_4) for brevity termed mixed oxides of nitrogen (MON). Table 5-3 presents the physical properties of the principal oxidizers containing oxygen.

5-4.4.1. Liquid Ozone (LOZ). Liquid ozone, for brevity designated as LOZ, is a deep blue liquid. It boils at $-111°C$, its density is 1.71 g/cc at $-183°C$ and it has a negative heat of formation (-30.3 kcal/mol at $-110°C$). Propellant systems based on LOZ give specific impulse values comparable to those based on liquid fluorine (see Table 5-1). LOZ is made by the silent discharge of electricity through oxygen gas. (28, 29) The O_3 molecule is thermally unstable, sensitive to shock, and these factors combined with its large oxidizing potential make LOZ hazardous to handle. It decomposes with explosive violence according to the equation

$$2 \ O_3 \rightarrow 3 \ O_2 \quad + 34.5 \ kcal$$

It is important to keep LOZ pure. Hence, it must be made from oxygen which is free of even traces of impurities. The sensitivity of LOZ can be reduced by making mixtures of LOZ in LOX. Thus a solution of LOX containing approximately 25 percent LOZ is quite stable to shock, and the mixture boils as a single phase at $-183°C$. Calculations show, however, that burning the 75LOX-25LOZ mixture with gasoline increases the specific impulse above that when LOX alone is used, by approximately 6 seconds. Since LOX is more volatile than LOZ (see Table 5-3), the 75-25 mixture tends on storage to increase in LOZ content due to the evaporation of LOX. When the LOZ concentration exceeds approximately 30 percent, explosions of extreme violence can result from contamination with minute traces of organic matter. (29)

Since LOZ has not as yet been effectively stabilized, and because of the small increase in performance with the 75LOX-25LOZ mixture, LOZ cannot be considered to be a promising oxidizer at this time.

5-4.4.2. Hydrogen Peroxide. The principal characteristics of concentrated solutions of H_2O_2 were presented in Paragraph 5-3.5 where its use as a monopropellant was discussed. Despite their relatively high freezing points, water solutions of H_2O_2 containing 90 percent or more H_2O_2 have been considered for certain applications. The high density, high boiling point, and good performance (see Table 5-1) obtainable with such solutions make them attractive as a replacement for liquid oxygen. In applications where a large value of density impulse is of importance, certain hydrogen peroxide propellant systems may be suitable. Furthermore, in a missile using hydrogen peroxide as the oxidizer, monopropellant runout can be employed. (12)

5-4.4.3. Nitric Acid. The following fuming nitric acids have been considered as oxidizers: white fuming nitric acid (WFNA), red fuming nitric acid (RFNA), and mixed acid (MA). The principal disadvantages of nitric acids are the tendency to decompose thermally, and their high corrosivity. These disadvantages introduce storage problems.

WFNA has been used in this country in several liquid propellant engines for rocket assisted take-off (RATO) and in-flight-thrust-augmentation (IFTA). Its composition is 98 percent HNO_3, 2 percent H_2O with traces of N_2O_4.

Considerable effort has been expended on improving the stability of fuming nitric acid and decreasing its corrosivity. The thermal decomposition of HNO_3 may be expressed by the equilibrium equation (30, 31)

$$2 \ HNO_3 \rightleftharpoons 2 \ NO_2 + H_2O + \tfrac{1}{2} O_2$$
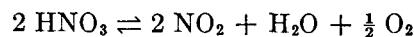
Studies of the above reaction show that its rate is slow at temperatures below $160°F$ but increases rapidly above that temperature. Because the oxygen gas formed is relatively insoluble in the acid very high storage pressures can be encountered where containers are nearly full. Moreover, since the NO_2 and H_2O are more soluble in the acid than the oxygen, the composition of the acid changes with the storage time within the range of the initial and equilibrium concentrations of NO_2 and H_2O. If the thermal decomposition is accompanied by corrosion of the container material, then the composition of the acid changes continuously in storage, which is undesirable. (32)

Although a great deal of effort has been expended, no inhibitor has been discovered for reducing the rate of thermal decomposition to a negligible value. Consequently, attention has been given to the use of additives for lowering the equilibrium decomposition pressure. (33, 36)

It is apparent from the decomposition equation for nitric acid that the addition of NO_2 and H_2O to the acid should decrease the amount of O_2 formed, since they appear in the equation, and consequently reduce the equilibrium storage pressure. A satisfactory red fuming nitric acid (RFNA) containing on a weight basis approximately 83-84 percent HNO_3, 14 percent NO_2 and 2 to 3 percent water, will reduce the oxygen pressure to less than 100 psia where filling voids are of the order of 10 percent. The latter storage pressure is satisfactory for many purposes.

It has been found that the addition of small amounts of hydrofluoric acid (HF) to fuming nitric acid will reduce its corrosion attack on certain stainless steels and aluminum alloys. (36)

TABLE 5-4. PHYSICAL PROPERTIES OF NITROGEN OXIDES

(Reference 23)

Name	Formula	Av. Molecular Weight $\overline{m}$	Density, ρ (@ temp. °C) (g/cc)	Freezing Point °C	Boiling Point °C	Heat of Formation Q_f (kcal/mol)	Stability at room temperature
Nitrous oxide	N_2O	44.02	1.226^{-89}	−102.4	−88.5	19.65	Stable
Nitric oxide	NO	30.01	$1.269^{-152.2}$	−163.6	−151.7	21.5	Stable
Nitrogen trioxide	N_2O_3	76.02	1.447^{20}	−102.3	3.5	10.3	Quite unstable
Nitrogen dioxide	NO_2	46.01	1.45^{20}	−11.2	21.2	7.96	Stable
Nitrogen tetroxide	N_2O_4	92.02	1.45^{20}	−11.2	21.2	2.24(g)	Stable in equilibrium with NO_2
Nitrogen pentoxide	N_2O_5	108.02	1.63^{18}	−32.4*	47	0.700(g)	Low stability
Nitrogen peroxide	NO_3	62.01	—	−142**	—	13.00(?)	Very unstable

(g) denotes gas.
* N_2O_5 sublimes and decomposes rapidly above room temperature.
** Solid NO_3 was trapped at −185°C but began decomposing rapidly at −143°C.

A fuming nitric acid having the weight composition of 83.5 percent HNO_3, 14 percent NO_2, 2 percent water, 0.5 percent HF, is known as either stabilized fuming nitric acid (SFNA) or inhibited fuming nitric acid (IFNA). SFNA freezes at −65°F, has a density of 1.56 g/cc at 20°C, and can be stored practically indefinitely at temperatures up to 160°F in either aluminum or stainless steel containers with no serious corrosion. And where the filling voids are in the order of 10 percent the equilibrium storage pressure does not exceed 100 psia.

SFNA is the only oxidizer now in use having a low freezing point, high density, reasonable vapor pressure at normal ambient temperatures, and low viscosity. Since propellant systems based on SFNA or RFNA (see Table 5-1) do not give as high specific impulse values as those based on either fluorine or LOX, SFNA appears to be best suited for applications where its physical properties and good storage properties are of such importance that the lower specific impulse is acceptable, for example, in ready tactical missiles of short and medium range.

5-4.4.4. Mixed Oxides of Nitrogen. Table 5-4 presents the physical properties of the seven known oxides of nitrogen; N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5, and NO_3. It is apparent from Table 5-4 that N_2O_3, N_2O_5, and NO_3 are too unstable under ordinary conditions to be considered as oxidizers for use in rocket jet propulsion engines. Of

the remaining oxides only nitrogen dioxide (NO_2) and nitrogen tetroxide (N_2O_4) have received consideration as oxidizers in liquid rocket bipropellant systems, and those appear together as an equilibrium mixture at ordinary temperatures. The term mixed oxides of nitrogen, denoted by MON, will be given to the equilibrium mixture. See Table 5-3 for the physical properties of MON. The principal advantage of MON is that at low concentrations of water (less than 0.1 percent by weight) it can be stored practically indefinitely in either mild steel or aluminum containers. Its two principal disadvantages are its high melting point (−11.3°C) and its extreme toxicity.

Although a number of freezing point depressants have been investigated, the most promising one is nitric oxide (NO). Because of the high volatility of the NO, the vapor pressure of solutions of NO in MON becomes quite high at a storage temperature of 160°F. Thus a solution containing 16.85 percent NO by weight has a freezing point of approximately −29°F, and a vapor pressure of approximately 240 psia. Reference 39 presents data on the freezing point and vapor pressure of solutions of NO in MON as a function of the NO concentration.

As noted above MON is extremely toxic. The maximum tolerable concentrations are quite small, 500 parts per million being rapidly fatal and exposure for 30 to 60 minutes to a concentration of 100 parts per million being dangerous. Since missiles using MON as the oxidizer could be filled

TABLE 5-5. PHYSICAL PROPERTIES OF OXIDIZING COMPOUNDS CONTAINING FLUORINE AND OXYGEN

Oxidizer	Av. Molecular Weight $\bar{m}$ (g/mol)	Density ρ (@ temp. °C) (g/cc)	Melting Point °C	Boiling Point °C	Heat of Vaporization Q_v (kcal/mol)	Heat of Formation Q_f (@ temp. °C) (kcal/mol)	Specific Heat C_p (@ temp. °C) (cal/mol °C)
F_2O	54	1.90^{-224}	-223.8	-144.8	2.65	-1.4^{-188}	11.3^{-188}
NOF	49	—	-132.5	-59.9	—	—	—
NO_2F	65	—	-166	-72.4	—	—	—
NO_3F	81	—	-175	-45.9	—	—	—

at the factory, thereby eliminating the need for handling it in the field, its toxicity should not rule it out as a possible oxidizer. Where space is limited, however, as on board a ship or submarine the dangers from accidental damage to a storage tank may be sufficiently great to prohibit its use. Recent experience with MON has been favorable from the standpoints of handling and hazard to personnel, hence MON must be given consideration in applications requiring storable oxidizers.

5-4.5. Oxidizers Containing Fluorine and Oxygen.

For fuels containing carbon and certain metals, such as boron, the maximum specific impulse is obtained with an oxidizer containing both fluorine and oxygen. The combustion products obtained by burning fuels containing the elements hydrogen, carbon, and boron are tabulated below.

Element	Combustion Products With oxygen	With fluorine
Hydrogen(H)	H_2O	HF
Carbon(C)	CO, CO_2	CF_4, CF_3, CF_2, CF
Boron(B)	B_2O_3	BF_3

The molecular weights of H_2O and HF are comparable, 18.016 and 20.008 respectively, but HF is much more stable thermally than H_2O. Hence, if the predominant constituent of a fuel is hydrogen, then it will give a larger specific impulse with fluorine than with oxygen as the oxidizer.

The molecular weights of CO and CO_2, on the other hand, are smaller than those of the fluorocarbon species. Hence, if a fuel has a large carbon content, it gives its largest specific impulse with oxygen as the oxidizer.

From the foregoing it appears that in the case of fuels containing the elements H and C, the maximum performance is obtained with an oxidizer containing both fluorine and oxygen, the

hydrogen reacting with the fluorine and the carbon with the oxygen. A similar situation occurs in the case of fuels containing boron. Calculations show that the maximum specific impulse is obtained with an oxidizer containing oyxgen and fluorine.

Table 5-5 presents the physical properties of some of the oxidizers which are compounds containing fluorine and oxygen. Table 5-3 presents the physical properties of a mixture containing 70 percent F_2 + 30 percent O_2, by weight.

5-4.5.1. Fluorine Monoxide.

Fluorine monoxide (F_2O) and the 70 F_2 + 30 O_2 mixture give reasonably high values of specific impulse with non-carbonaceous fuels, and also with fuels containing boron. F_2O has a higher boiling point than the aforementioned mixture and is easier to handle. Since it is made from fluorine and the process gives a low yield of F_2O, it is more expensive than either fluorine or fluorine-oxygen mixtures. Moreover, there is the advantage that the proportions of a fluorine-oxygen mixture can be adjusted to the carbon-hydrogen ratio of a carbonaceous fuel.

5-4.6. Perchlorofluoride (ClO_3F).

This oxidizer is a recent development. Its basic advantages are that it is compatible with most materials of construction, and its density is relatively high (1.43 g/cc at 60°F). Its principal disadvantages are the HCl and HF in the exhaust products, its low availability, and high cost.

From an overall standpoint ClO_3F does not appear to offer any substantial advantages over oxidizers such as H_2O_2, SFNA, and MON. Moreover, its high vapor pressure is a disadvantage in using it in prefueled missiles, and also in turbopump pressurizing systems without refrigerating the ClO_3F.

TABLE 5-6. PHYSICAL PROPERTIES OF SOME LIQUID ORGANIC AND NITROGEN HYDRIDE FUELS

Fuel	Av. Molecular Weight $\bar{m}$	Specific Gravity ρ (@ temp. °C)	Melting Point °C	Boiling Point °C	Heat of Formation Q_f (@ temp. °C) (kcal/mol)	Specific Heat C_p (@ temp. °C) (Btu/lb °F)	Viscosity μ (@ temp. °C) (Centipoise)
NH_3	17	0.61^{20}	−78	−33	11.0^{25}	1.13^{20}	0.48^{-70}
N_2H_4	32	1.01^{15}	1.4	114	-12.0^{25}	0.74^{25}	1.2^{5}
C_2H_5OH	46	0.79^{20}	−117	78.5	66.3^{25}	0.54^{3}	8.4^{-59}
JP4	—	0.76^{20}	−60	(69)	—	—	10^{-55}
UDMH	61.1	0.79^{22}	−57	63.0	-12.7^{25}	0.65^{20}	4.0^{-50}
DETA	103.2	0.96^{20}	−39	207	15.4^{25}	—	100^{-18}

5-5. FUELS FOR LIQUID BIPROPELLANT SYSTEMS

The factors to be considered in selecting a liquid chemical compound which will be a satisfactory rocket fuel have been discussed in paragraph 5-1. From a performance viewpoint they must have high enthalpies of combustion and yield gas products having a low value of molecular weight $\bar{m}$. As pointed out earlier, while the number of practical oxidizers is limited, there are many fuels suitable for rocket propellant systems. For convenience of discussion rocket fuels will be grouped into the following classes:

1. Liquid hydrogen and light elements
2. Organic fuels
3. Nitrogen hydrides.

Table 5-6 presents the physical properties of the more important organic fuels and the nitrogen hydrides.

5-5.1. Liquid Hydrogen and the Light Elements.
(44, 45) Liquid hydrogen gives the largest values of I_s of all fuels, and with all liquid oxidizers (see Table 5-1). Because of its low boiling point (−423°F) its handling and storage is a difficult problem, and its small specific gravity (0.07 at −423°F) is a disadvantage. It must be handled with care because hydrogen gas forms explosive mixtures with air. The limited experience with liquid hydrogen indicates that it can be handled in much the same manner as liquid oxygen. It appears that the use of liquid hydrogen will be limited to certain special applications for which a high specific impulse is of prime importance.

The use of light metals as fuels for rocket motors appears attractive because when they combine with oxygen to form oxides they have large enthalpies of combustion. Since the combustion products must have a low molecular weight, only the light metal elements such as lithium, beryllium, boron, and aluminum are of interest. In all cases the combustion temperatures are very high and when allowance is made for the evaporation and dissociation of the oxides, it is found that they give major gains in specific impulse. Figure 5-2 is a bar graph comparing the enthalpies of combustion of several fuels.

A disadvantage in the use of light metals as rocket fuels is that their oxides in the exhaust make it smoky. Moreover, beryllium is extremely toxic, and lithium is quite scarce.

5-5.2. Borohydrides.
Table 5-7 presents some of the physical properties of the borohydrides. Calculations show that after hydrogen the next highest performance fuels are the boron compounds containing hydrogen. In this country much research has been devoted to diborane (B_2H_6) and pentaborane (B_5H_9).

The borohydride fuels when reacted with F_2O, F_2, O_2, and H_2O_2 offer theoretical maximum specific impulses, based on mobile equilibrium, of approximately 300 sec. (12) At present they are in short supply and also have certain undesirable properties. Thus, diborane (B_2H_6) boils at −135°F and is unstable. It decomposes slowly to form large quantities of hydrogen. Pentaborane (B_5H_9) has more favorable properties than diborane. It boils at 140°F, and its rate of decomposition at room

PROPULSION AND PROPELLANTS

Btu/lb x 10³   SOURCE: OLIN MATHIESON CHEMICAL CORP.

ENTHALPY OF COMBUSTION
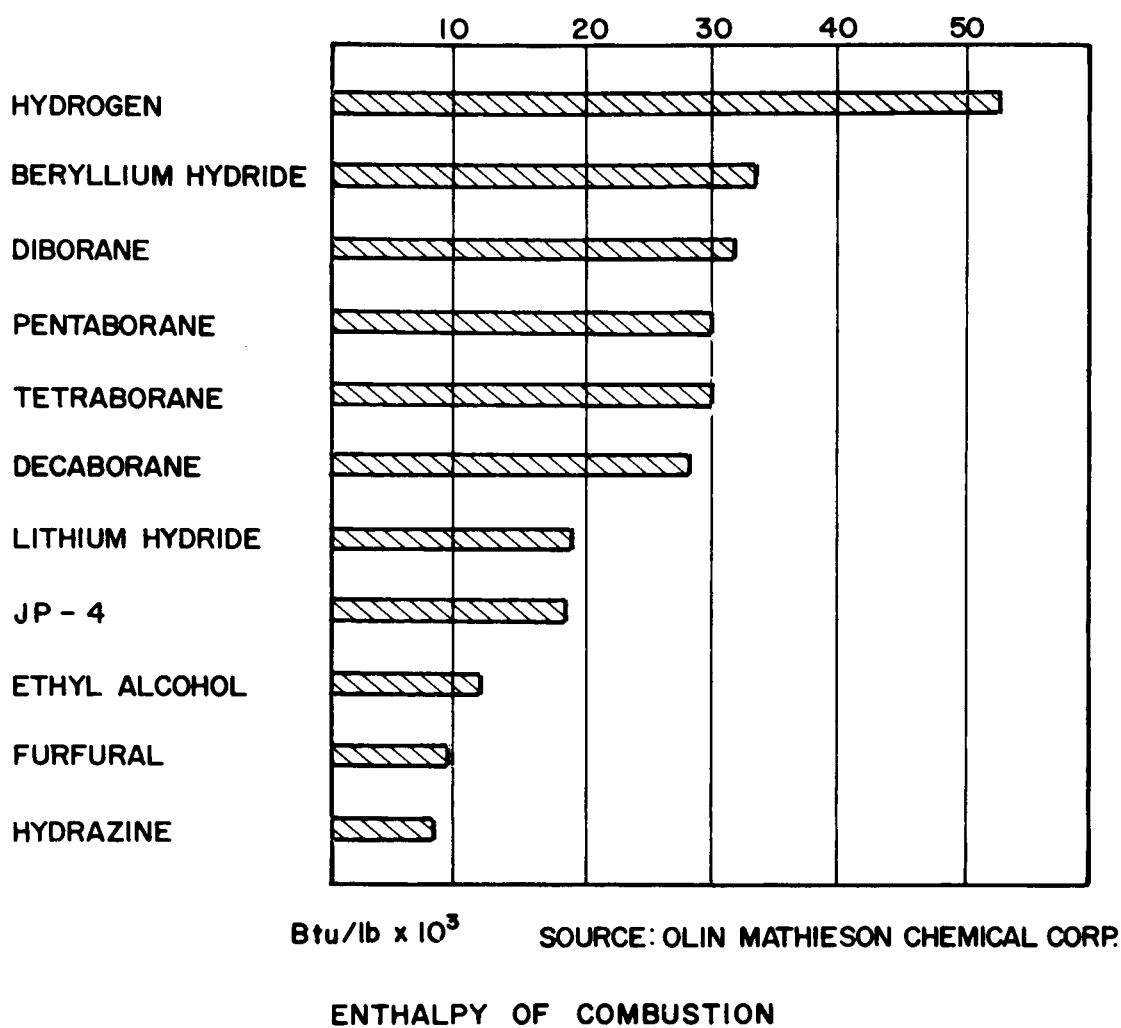
(Taken from Reference 46)

Figure 5-2. Enthalpy of Combustion in Btu/lb of Several Fuels with Oxygen

TABLE 5-7. PHYSICAL PROPERTIES OF BOROHYDRIDE FUELS

(Reference 46)

Fuel	Formula	Av. Molecular Weight m	Density ρ (g/cc)	Boiling Point °F	Melting Point °F
Diborane	B_2H_6	27.7	0.43	−135	−265
Pentaborane	B_5H_9	63.2	0.61	140	−52
Decaborane	$B_{10}H_{14}$	122.3	0.94	415	211

temperature is comparatively slow. Decaborane is a solid at room temperature.

Neither pure diborane nor pure pentaborane appear to ignite spontaneously when in contact with air. Apparently they decompose to form self-igniting boron hydrides, and the mixture increases in inflammability. None of the borohydrides decompose explosively, and they decompose slowly even when heated. Violent decomposition can occur when they are in contact with other metals.

Considerable effort is being expended on the development of boron compounds for use as additives to hydrocarbon fuels for use in rocket engines and air-breathing engines. It is claimed that when reacted with oxygen these compounds have 60 percent greater heat of combustion than jet engine fuel.

If the borohydrides can be produced in large quantities at a reasonable price, they will be of interest as rocket fuels.

5-5.3. Organic Fuels. All liquid fuels containing carbon and hydrogen are termed organic fuels, and several have been investigated for use in liquid rocket bipropellant systems. The discussions here will be limited to those organic fuels that are of current interest:

1. Ethyl alcohol
2. Light hydrocarbons (JP fuels)
3. Unsymmetrical dimethylhydrazine (UDMH)
4. Diethylenetriamine (DETA).

5-5.3.1. Ethyl Alcohol. Ethyl and methyl alcohols are the only lower alcohols which have been investigated and used as fuels in rocket engines. They are slightly inferior to the hydrocarbons in performance. Ethyl alcohol was used in the German V-2 missile and has been used in the Redstone missile.

Ethyl alcohol (C_2H_5OH), also called ethanol, melts at −117°C and boils at 78.5°C. It is plentiful and inexpensive and is a good regenerative coolant. Its main disadvantage is its low specific gravity (0.79 at 20°C). It is compatible with most normal construction materials, is non-toxic, and non-corrosive. Hot ethanol is said to etch aluminum. With LOX the maximum obtainable specific impulse is approximately 240 sec (based on frozen composition) and its combustion is smooth. Ethanol is non-hypergolic with most oxidizers.

5-5.3.2. Light Hydrocarbon Fuels. In this group are those mixtures of aromatics, olefins, paraffins, and naphthenes that are termed jet engine fuels, and are designated by "JP" with a numerical suffix. In general, they have a carbon-hydrogen ratio of approximately 6 and a lower heating value of approximately 18,500 Btu/lb. Table 5-8 presents the physical properties of several such fuels.

The JP fuels are plentiful and inexpensive, have good handling characteristics, are compatible with most of the common materials of construction, are non-toxic, have good storage properties, and give reasonably high values of specific impulse either with oxygen or mixtures of oxygen and fluorine.

The disadvantages of JP fuels are low specific gravity and their tendency to crack and deposit solids when used as regenerative coolants. They also tend to deposit solids in the nozzles of the gas turbine for driving propellant pumps when used with LOX in fuel-rich reactions to produce gases for driving the gas turbine.

With nitric acid and MON, the JP fuels give low values of I_s and the combustion is apt to be rough. It is found advantageous to employ additives to the JP fuel when it is used with either SFNA or MON to improve the combustion characteristics.

TABLE 5-8. PHYSICAL PROPERTIES OF LIGHT HYDROCARBON LIQUID FUELS

(From Reference 46)

Hydrocarbon Fuel	Distillate Range, °F	Gravity deg, API	Freeze Point °F, max	Flash Point °F, min	General Description
JP–1	400–570	50–60	−76	110	Low freeze kerosene
JP–3	150–500	50–60	−76	NR[1]	High vapor pressure JP–4
JP–4	200–550	45–57	−76	NR	Wide-cut gasoline
JP–5	350–550	36–48	−40	140	High flash kerosene
JP–6	250–550	37–50	−65	NR	Thermally stable kerosene
RJ–1	400–600	32.5–36.5	−40	190	Thermally stable, heavy kerosene
RP–1	380–525	42–45	−40	110	Pure, light cut kerosene

[1] NR: No requirement.

In applying JP fuels to long range missiles, problems arise due to the variations in the density and composition of the fuel. These changes materially affect the performance of the engine and also complicate the accurate fueling of the missiles (see Paragraph 5-2.4).

The JP fuels are non-hypergolic with most liquid oxidizers.

5-5.3.3. Unsymmetrical Dimethylhydrazine (UDMH).

This fuel is currently being produced in relatively large quantities under the trade name "dimazine." UDMH possesses excellent physical properties and is compatible with common construction materials. It burns smoothly with most oxidizers and gives relatively high performance (see Table 5-1). Its specific gravity is rather low (0.79).

UDMH is thermochemically unstable and has the potentialities of being used as a monopropellant, but this requires more investigation. It is hypergolic with fuming nitric acids at very low temperatures and gives extremely short ignition delays, approximately 2 milliseconds at −75°F. It appears to be the most suitable fuel for use with stabilized (red) fuming nitric acid (SFNA), because of its excellent combustion characteristics with that oxidizer.

5-5.3.4. Diethylenetriamine (DETA).

There are several organic amines which may be useful as rocket fuels. Some of them give reasonably high values of specific impulse and have good physical properties. (12) All of them are toxic to some degree. Since they are reasonably stable at high temperatures they may be good regenerative coolants.

DETA has a high specific gravity (0.96 at 70°F), is available in large quantities at fairly low cost, has a moderately low freezing point (−38°F), and gives a larger I_s with LOX than the JP fuels give. It also gives better general performance with fuming nitric acid (FNA), being hypergolic with very short ignition delays. It can be substituted for the JP fuels in missiles designed originally for JP fuels, without introducing any major problems. Because of the greater density of DETA the performance of the missile is improved. DETA is compatible with common construction materials and has good storage, handling, and heat transfer characteristics.

5-5.4. Nitrogen Hydrides.

Two stable nitrogen hydrides are of interest as rocket fuels: ammonia (NH_3), and hydrazine (N_2H_4). Their physical properties are presented in Table 5-6.

5-5.4.1. Anhydrous Ammonia.

Ammonia (NH_3) is available commercially in large quantities, is cheap, and can be stored in steel containers. It is moderately toxic but its presence is easily detected. NH_3 gives reasonably high values of specific impulse with most oxidizers and is non-hypergolic with most of them.

Ammonia has a low specific gravity (0.61 at 70°F) and a high vapor pressure (493 psia at 160°F). When used as a liquefied gas the vapor pressure problem is eliminated by applying refrigeration. Its low density detracts from its usefulness as a rocket fuel, but it appears to be of interest when used with fluorine as the oxidizer. Information is lacking, however, on the capabilities of ammonia as a regenerative coolant under the high

heat flux conditions occurring when it is burned with fluorine.

Ammonia gives smooth combustion with WFNA and RFNA. The starting and stopping of the rocket engine is also smooth. Although it is non-hypergolic with FNA, ignition can be made hypergolic by causing liquid NH_3 to flow over a small amount of lithium before entering the combustion chamber.

5-5.4.2. Hydrazine. The physical characteristics of hydrazine (N_2H_4) as well as its storage and handling characteristics are discussed in paragraph 5-3.6, where its use as a monopropellant was described. Reference to Table 5-1 shows that when used as the fuel in a bipropellant system it gives high values of specific impulse with every oxidizer. Its main disadvantage is its high freezing point (35°F), and the lack of adequate information as to its characteristics as a regenerative coolant. In a missile application it offers the advantage of monopropellant runout.

Hydrazine is hypergolic and gives small ignition delays with all of the common oxidizers except LOX. It appears to be the best fuel for use with liquid fluorine, ClF_3, H_2O_2, and MON. It is worth noting that the high freezing point of N_2H_4 (35°F) is of the same order of magnitude as the

freezing points of N_2O_4 (12°F) and H_2O_2 (30°F).

5-5.4.3. Mixtures of Hydrazine and Ammonia. There is interest in N_2H_4-NH_3 mixtures because they have certain properties which are superior to those of the individual constituents. (12) It has been pointed out that NH_3 is cheap, plentiful, stable under storage conditions, has a low freezing point (−78°C), gives reasonable values of specific impulse, but has a low density and a high vapor pressure. Hydrazine, on the other hand, is relatively expensive and has a high freezing point (35°F), but its density is high and it gives larger values of specific impulse than does NH_3. By adding NH_3 to N_2H_4, a mixture can be made that has a reasonably low freezing point, good performance, and a reasonable density. For example, a mixture of 38 percent by weight NH_3 in N_2H_4 freezes at −30°F, while the 50 percent NH_3-50 percent N_2H_4 mixture freezes at −40°F. As the NH_3 content is increased the vapor pressure increases, especially at high temperatures. For 36 percent NH_3 in N_2H_4, the vapor pressure at 158°F is 18.5 atm. The mixture 37 percent NH_3, 59 percent N_2H_4, and 4 percent water gives an experimental value of specific impulse of approximately 280 sec when burned with liquid fluorine at 300 psia combustion pressure.

5-6. REFERENCES

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Chapter 6

PROPERTIES AND CHARACTERISTICS OF SOLID PROPELLANTS

Due to the significant advances made in the technology of solid propellants, they must be given consideration in missile applications that once were deemed suitable only for liquid propellant rocket engines. (1, 22) While the emphasis in this section will be on composite propellants, great strides have been made in the development of double-base propellants, and for several applications they are superior to composite propellants.

6-1. DESIRED CHARACTERISTICS FOR A SOLID PROPELLANT

The factors to be considered in judging the merit of a solid propellant are discussed below. (1, 3)

6-1.1. Specific Impulse (I_s). The specific impulse should have the largest possible value since the ideal burnt velocity V_{bi} (see equation 3-36) is directly proportional to I_s. For modern composite propellant formulations the basic ingredients are such that the combustion gases are compounds of the following elements: carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and chlorine (Cl). For C-H-N-O-Cl systems the maximum obtainable specific impulses are in the range 240 to 250 sec. For a given composite propellant the specific impulse increases with the ratio of oxidizer to binder. There is a limit, however, to the quantity of oxidizer which can be incorporated into a given binder (2) (see Paragraph 6-1.4). Various light metals are added to both composite and double-base propellant formulations for increasing the specific impulse. (21)

6-1.2. Density of Propellant. The propellant should have a high density in order to provide a large amount of propellant in a small space, and thereby reduce the dimensions of the rocket motor. For most composite solid propellants the densities range from 1.65 to 1.70 g/cc compared to approximately 0.94 g/cc for liquid propellant systems.

6-1.3. Controllable Linear Burning Rate (r_o). It is desirable to be able to control the linear burning rate r_o, over a wide range. With current composite solid propellants, linear burning rates from approximately 0.1 in/sec to 2.0 in/sec are obtainable. A wide range of available burning rates increases the design flexibility of solid propellant rocket motors. Also, it is desirable that the linear burning rate be rather insensitive to the combustion pressure.

6-1.4. Physical Properties. The important physical properties are tensile strength, elongation, adhesion, and fluidity. A high tensile strength is needed so that the grain will not deform under the required operating conditions. A high percent elongation is necessary so the grain will not crack when it is deformed by either pressure or temperature changes. The requirement of reasonably high tensile strength and elongation limit the oxidizer-binder ratio.

In case-bonded designs it is essential that the propellant grain adhere strongly to the metal case and that the bond be not broken either by the expansions or contractions of the case.

In the case of castable composite propellants the oxidizer-binder slurry must be able to flow readily into the chamber wherein it is to be cast and cured. The fluidity of the slurry depends upon the oxidizer-binder ratio and the particle size and particle size distribution of the oxidizer. This consideration also limits the useful oxidizer-binder ratio.

It is desirable that the propellant have good physical properties over the temperature range -65 to $+165°F$, and be able to withstand temperature cycling between those limits. (4)

6-1.5. Chemical Stability. High chemical stability is desirable so that the solid propellant will have good aging characteristics, that is, performance should not deteriorate with long time storage.

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6-1.6. Toxicity. It is desirable that the propellant be safe to handle and that its combustion products be non-toxic and not linger around the launching site.

6-1.7. Explosive Hazard. The propellant should be safe to handle using well known, and more or less conventional procedures. It should have a relatively high ignition temperature and not burn readily at low pressures. However, it should ignite readily when fired by the igniter.

6-1.8. Smoke. For many applications it is desirable that the exhaust be smokeless, that is, there should be no solid materials in the exhaust gases.

6-1.9. Shock Sensitivity. It is desirable that the propellant shall not detonate due to either mechanical or thermal shock.

6-1.10. Availability of Raw Materials. If the propellant will be used in large quantities during an emergency the raw materials from which the binder and oxidizer are made should be available in abundant quantities.

6-1.11. Fabrication and Process Control. The propellant should be compatible with the usual construction materials, and should lend itself to process control methods for assuring product uniformity in all respects when produced in large quantities.

6-1.12. Cost. It is desirable, of course, that the propellant be relatively inexpensive.

The propellant should have a low shrinkage during cure and its curing exotherm should be low. A low curing temperature enhances safety in the manufacturing process.

6-2. OXIDIZERS FOR COMPOSITE PROPELLANTS

As in the case of liquid bipropellant systems, there are only a few oxidizers which are useful in the manufacture of solid composite propellants. The useful oxidizers and the weight percent of oxygen available in them are presented in Table 6-1.

TABLE 6-1. OXIDIZERS FOR USE IN COMPOSITE PROPELLANTS

Name	Formula	$\overline{m}$	% Oxygen Available
Ammonium nitrate	NH_4NO_3	80.05	20
Ammonium perchlorate	NH_4ClO_4	117.49	34
Potassium nitrate	KNO_3	101.10	39.5
Potassium perchlorate	$KClO_4$	138.55	46.5
Lithium perchlorate	$LiClO_4$	106.40	60.0

There is a large background of experience with all of the oxidizers listed in Table 6-1, except lithium perchlorate.

All perchlorate oxidizers produce hydrochloric acid in the exhaust gas which condenses into a fog on a moist day. The gases from a propellant based on $KClO_4$ are smoky because they contain condensed potassium chloride which is a white powder. Practically all of the high performance castable composite propellants are based on ammonium perchlorate as the oxidizer.

Propellants based on metallic nitrates as oxidizers, such as KNO_3 or $NaNO_3$, produce smoky exhausts. A great deal of effort has been expended on the development of propellants based on ammonium nitrate because of its abundance, low cost, and its non-toxic, smokeless exhaust. Due to its low available oxygen content and the effect of temperature on its crystalline structure, it is difficult to make a high performance castable propellant having good rheological (plastic) properties using NH_4NO_3 as the oxidizer.

6-3. FUELS FOR COMPOSITE PROPELLANTS

As pointed out in paragraph 2-3.4, the fuel for a composite solid propellant serves as the binder for the oxidizer particles. Several organic materials have been investigated as possible fuels. Those used in modern formulations are elastomeric monomers which, after being thoroughly mixed with the oxidizer, polymerize during the curing process. In general, the curing process is exothermic. Of the large number of organic binders which either have been or are being investigated, those receiving the greatest development effort are listed in Table 6-2.

TABLE 6-2. BINDERS FOR COMPOSITE PROPELLANTS

Binder	Propellant manufacturer
polysulfides	Thiokol Chemical Corp.
polyurethanes	Aerojet-General Corp.
butadiene pyridine copolymers	Phillips Petroleum Co.
butadiene-acrylic acid copolymers	Thiokol Chemical Corp.
petrinacrylate	Rohm and Haas, Redstone Arsenal

All of the binders listed in Table 6-2 have been used in making castable propellants except the butadiene pyridine copolymers; these have been used for making molded propellants principally with NH_4NO_3 as the oxidizer.

It is desirable that the binder contain a small amount of oxygen so that a closer approach to stoichiometric oxygen balance can be achieved, and not have the solid oxidizer content become so large that the propellant will have either poor rheological or mechanical properties.

6-4. BALLISTIC PROPERTIES OF SOLID PROPELLANTS (1, 5, 6)

The flight characteristics of a ballistic missile depend (among other things) on the performance of the propellant. Important flight performance (ballistic) properties are described in the following paragraphs.

6-4.1. Linear Burning Rate.
A solid propellant burns at its surface but the exact combustion mechanism is not completely understood. As the burning proceeds, the burning surface recedes in a direction perpendicular to itself. The rate at which the burning surface recedes is called the linear burning rate and is denoted by r. The burning rate depends in general on the propellant formulation and the conditions under which it is burned: it is a characteristic property of the propellant. For a given propellant, the burning rate is a function of the combustion pressure p_c, the propellant temperature t_p, the velocity of the combustion gas parallel to the burning surface V_g (for an end-burning grain $V_g = 0$), and the elapsed time τ after the grain is ignited. However, for a material to be a satisfactory solid propellant for a rocket engine, its linear burning rate must be independent of the time. Furthermore, the influence of V_g on

the linear burning rate is a secondary effect which gives rise to erosive burning which is discussed in paragraph 6-4.4.1. Since the experiments for measuring the burning rates of propellants can be conducted with $V_g = 0$, with end-burning grains for example, the following functional equation may be written for the linear burning rate:

$$r_O = F\ (p_c,\ t_p) \qquad (6\text{-}1)$$

where $r_O = r =$ linear burning rate for $V_g = 0$.

The form of the functional relationship expressed by equation (6-2) is determined experimentally. In the experiments t_p, the temperature of the propellant prior to ignition is held constant. Experiments show that for a fixed value of t_p, the relationship between p_c and r_O can be represented by

$$r_O = c\ p_c^n \qquad (6\text{-}2)$$

where c and n are determined experimentally.

Equation (6-2) is known as Saint Robert's law, and in applying that law it is assumed that the pressure exponent n is independent of p_c and t_p, while the burning-rate coefficient c depends on t_p and is independent of p_c. The exponent n, for most solid propellants, has a value between approximately 0.1 to 0.8. There are some double-base propellant formulations, however, for which n is zero and even negative over a usable pressure range.

The burning rates of modern castable composite propellants, based on ammonium perchlorate as the oxidizer, can be varied over a wide range by means of additives. For large solid propellant motors, a low burning rate with a small pressure exponent is desirable.

The weight rate of propellant consumption, assuming steady operation, is given by equation (3-17) which is rearranged here for convenience. Thus

$$\dot{W} = C_w p_c A_t \quad \text{(lb/sec)} \qquad (6\text{-}3)$$

In terms of the linear burning rate r_O

$$\dot{W} = r_O\ S_p\ \gamma_p \quad \text{(lb/sec)} \qquad (6\text{-}4)$$

where

$A_t =$ throat area of exhaust nozzle, sq in

$S_p =$ burning area of propellant, sq in

$\gamma_p =$ specific weight of propellant, lb/cu in

Figure 6-1 presents linear burning rate data r_O, at 60°F, for several composite propellants made by
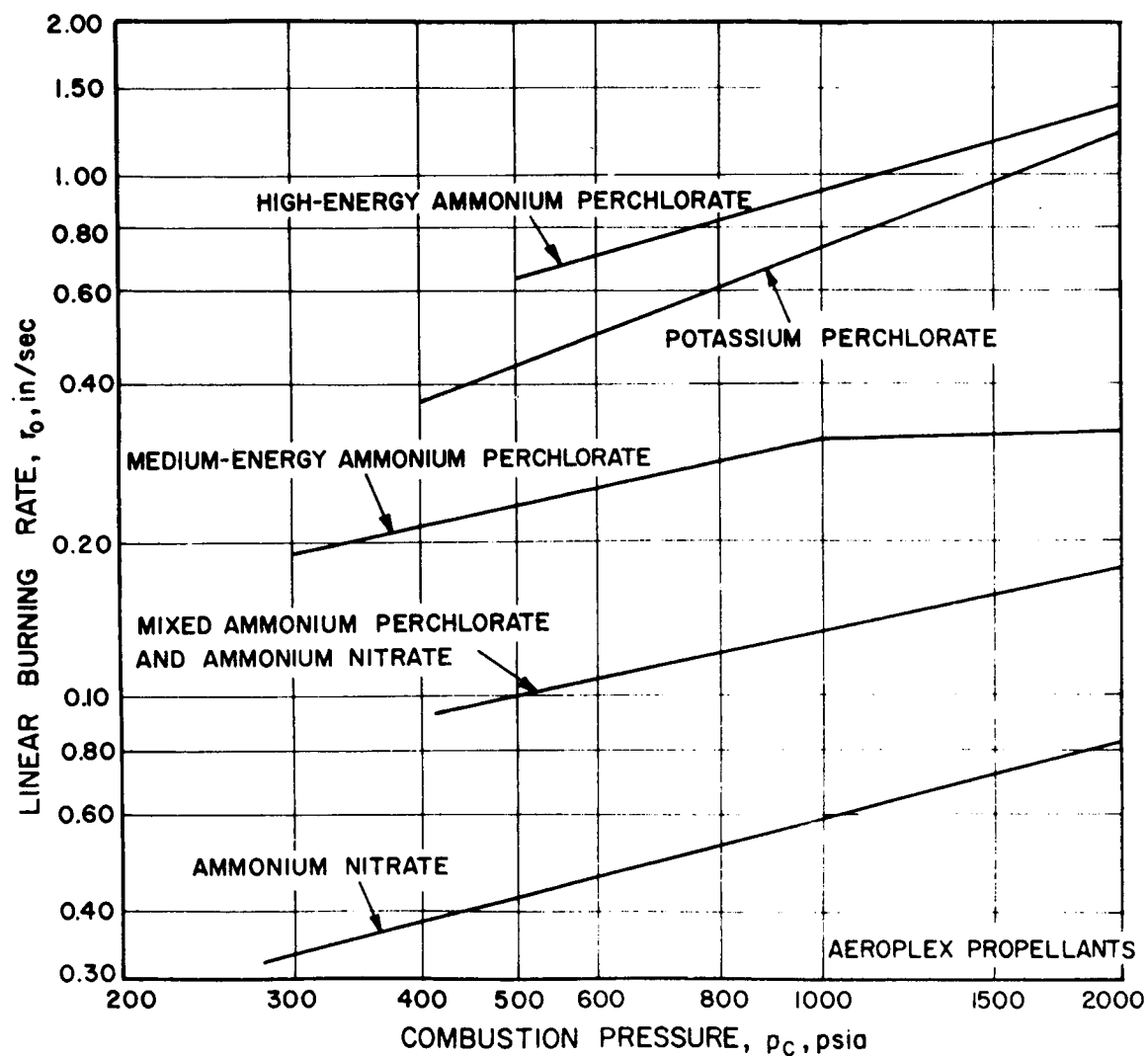
Source: Aerojet-General Corporation

(Taken from Reference 1)

Figure 6-1. Burning Characteristics of Several Heterogeneous Propellants at 60° F

compounding the same binder (fuel) with different amounts and kinds of organic oxidizers.

6-4.2. Propellant Area Ratio and Equilibrium Combustion Pressure. (1, 7) Under steady state operating conditions, at constant t_p, the combustion pressure remains constant and is termed the equilibrium combustion pressure. Let

$$K_n = \frac{S_p}{A_t} = \text{propellant area ratio} \quad (6\text{-}5)$$

where A_t = nozzle throat area (area of the cross-section of the throat of the exhaust nozzle).

The equilibrium combustion pressure p_c is given by

$$p_c = \left[\frac{K_n \, c\Delta\gamma}{C_{\dot{w}}} \right]^{1/(1-n)} \quad (6\text{-}6)$$

where $\Delta\gamma = \gamma_p - \gamma_0$.

Equation (6-6) shows that the propellant area ratio K_n exerts a predominant influence on the equilibrium combustion pressure. Since n is less than unity (except for the specific double-base powder formulations mentioned in paragraph 6-4.1) the exponent $1/(1-n)$ is always larger than unity. Consequently, an increase in K_n results in a much larger increase in p_c. Consequently, the value of K_n must be held within close limits if the design value for p_c is to be realized. It is because of the strong dependence of p_c on K_n, and in the interest of decreasing the sensitivity of p_c to minor variations in K_n, that a small value for the pressure exponent n is highly desirable.

For a fixed propellant temperature t_p, experiments demonstrate that the nozzle area ratio K_n can be related to the combustion pressure p_c by the relationship (1)

$$K_n = bp_c^m \quad (6\text{-}7)$$

where the exponent m is independent of t_p and the coefficient b is a function of t_p.

The relationship between the weight flow coefficient C_w and p_c can be represented by an empirical equation of the form

$$C_w = hp_c^q \quad (6\text{-}8)$$

For every solid propellant there is a value of combustion pressure, called the combustion limit, below which stable combustion is not possible.

Consequently, the propellant area ratio K_n must have a value such that it will give a combustion pressure larger than the combustion limit. The latter must be determined experimentally.

If K_n is increased continually for a given propellant the pressure also increases until finally a value is reached which, if exceeded, causes the combustion pressure to increase practically beyond bounds. This value of the combustion pressure is called the pressure limit.

6-4.3. Effect of Propellant Temperature. The temperature of a solid propellant affects its general physical characteristics and its burning rate. At low propellant temperatures the elastic properties of practically all solid propellants become poor, and in some cases the grain may become so brittle that it may crack when subjected to either shock or temperature cycling. Differences in the thermal expansion of the metal case, the liner of a case-bonded grain, and of the propellant may cause the grain to crack. When the flame reaches the crack there is a large increase in the burning surface with a corresponding increase in K_n. As a result the combustion pressure may reach prohibitive values.

Certain propellants become more difficult to ignite as the propellant temperature is lowered thereby increasing the ignition delay (time elapsed between firing the igniter and complete ignition of the burning surface).

At high propellant temperatures above 140°F many solid propellants tend to soften and become plastic. They may not be able to withstand the sudden pressure application during ignition without appreciable deformation of the grain.

Some propellants are subject to cold flow or slump when stored at the higher ambient temperatures, changing the configuration of the grain and hence the performance of the rocket motor.

Because of the influence of the propellant temperature upon the physical characteristics of a solid propellant, it is important that serious attention be given to the temperature limitations which are recommended for solid propellant rocket motors during their storage and handling.

6-4.3.1. Temperature Sensitivity. The linear burning rate for a given propellant burning with a fixed value of K_n is affected by the propellant temperature t_p. In general, r_0 decreases if t_p is decreased and vice versa. The effect of t_p on r_0 for

a solid propellant is termed temperature sensitivity. (1, 8)

It is customary to express the temperature sensitivity of the ballistic parameters (r_o, p_c, F), in percent change per degree Fahrenheit from their values at some standard temperature $t_p = t_o$ (usually $t_o = 60°F$), under a constant condition of K_n. When $t_p > t_o$ the parameters have values larger than those corresponding to $t_p = t_o$, and vice versa.

Thus the temperature sensitivity coefficient for the linear burning rate, denoted by π_{ro} is defined by

$$\pi_{ro} = \frac{1}{r_o} \left[\frac{\partial r_{o_i}}{\partial t_p} \right]_{K_n} \qquad (6\text{-}9a)$$

where $(\partial r_o / \partial t_p)_{K_n}$ is the rate of change for the linear burning rate with temperature for a constant value of K_n.

For thrust F and combustion pressure p_c, one can write

$$\pi_F = \frac{1}{F} \left[\frac{\partial F}{\partial t_p} \right]_{K_n} = \frac{\text{thrust temperature}}{\text{sensitivity coefficient}} \qquad (6\text{-}9b)$$

and

$$\pi_{p_c} = \frac{1}{p_c} \left[\frac{\partial p_c}{\partial t_p} \right]_{K_n} = \frac{\text{combustion pressure}}{\text{temperature sensitivity}}_{\text{coefficient}} \qquad (6\text{-}9c)$$

The temperature sensitivity of a solid propellant and the application of the motor must be given careful consideration. In the case of a ballistic missile the different burning rates at different propellant temperatures cause the trajectories to vary from the standard ones, and can cause large divergences unless they are taken into account. The temperature sensitivity of solid propellants has been one of the serious disadvantages in the application of solid propellant rocket motors to ballistic missile propulsion. For many applications the cold weather problem can be circumvented by using heating blankets to keep the propellant at a specified temperature. Many schemes have been suggested for overcoming the adverse effects of temperature sensitivity upon the performance of ballistic missiles, but all of them introduce undesirable complications which may decrease the reliability of the missile. Since it is highly desirable

to solve the problem by developing solid propellants having insignificant temperature sensitivity, research in this area should receive strong support.

6-4.4. Combustion of Solid Propellants.
There are two combustion phenomena of particular significance to the performance of solid propellant rocket engines; erosive burning, and resonant burning.

6-4.4.1. Erosive Burning.
As mentioned in paragraph 6-4.1, the velocity of combustion gases parallel to the burning surface has an effect upon the linear burning rate called erosive burning. Although the exact mechanism whereby the burning rate increases as the combustion gas velocity is increased is only incompletely understood, its occurrence has been observed. Since erosive burning increases with increased gas velocity, the effect is more pronounced in a restricted flow cross-section such as the nozzle end of an internal-burning case-bonded grain during the initial phases of combustion. Erosive burning is evidenced by peaks in the combustion pressure during the early phase of the combustion of the propellant grain.

No completely satisfactory relationship has been developed for correlating data on the erosive burning of solid propellants. (9, 20) It is customary, however, to express the erosive burning of a solid propellant in terms of the erosion ratio ϵ as a function of the gas velocity V_g, where

$$\epsilon = r/r_o \qquad (6\text{-}10)$$

and r is the linear burning rate with erosive burning.

From the limited data available it appears that ϵ increases with the gas velocity V_g when the latter is above some minimum value. Furthermore, it appears that ϵ is larger for the slower-burning propellants, and is independent of t_p. More research is required to obtain a better understanding of, and more reliable data on, erosive burning. When it becomes available this missing information will be of great value in developing the large grains required for the larger ballistic missiles.

6-4.4.2. Resonant or Sonant Burning.
It has been observed that the combustion pressure, and consequently the thrust, of an internal-burning

solid propellant grain may increase practically instantaneously to several times its equilibrium value for no apparent reason. (10, 19) This phenomenon has been termed resonant burning, sonant burning, and combustion instability. The few published experimental results indicate that sonant burning is always accompanied by dangerous high-frequency, large-amplitude oscillations in the combustion pressure, with the burning rate increasing to as much as two and one-half times its steady state design value.

Currently there is no satisfactory theory for explaining the cause of sonant burning, or for predicting whether or not it will occur in a specific solid propellant rocket motor design. Recent experiments have shown that the addition of small amounts of either aluminum or aluminum oxide to either double-base or composite propellant formulations effectively reduces or completely eliminates resonant burning. (21) Unfortunately, there is at present no satisfactory explanation of the mechanism of resonant burning for solution of the problem.

6-5. HEAT TRANSFER IN SOLID PROPELLANT ROCKET MOTORS

Heat is transferred from the hot combustion gases to those surfaces in contact with them by convection, radiation, and conduction. Of those modes of heat transfer, convection is the dominant one. The quantity of heat transferred to the surfaces in contact with the combustion gases is a complex function of several variables, such as the flame temperature, the physical properties of the combustion gases, the grain design, the combustion pressure, and the configuration of the motor case and exhaust nozzle. Since the total weight of the inert metal parts must be held to a minimum for a ballistic missile engine, the internal-burning case-bonded grain design is favored since only the fore-cap and nozzle are exposed to the hot gases. In general, for short burning durations the problems due to heat transfer are not serious. For applications such as ballistic missiles where the duration of burning is relatively long, the problems arising from heat transfer are difficult and challenging.

Because of the extremely high mass velocity of the combustion gases and their high temperature (4500 to 5500°F for high performance propellants), the heat transfer rates to the aft-cap and nozzle are large, but those in the nozzle throat are several-fold those for the aft-cap. The aft-cap is protected from reaching dangerously high metal temperatures by protecting it with layers of a suitable insulating material. In general, the exhaust nozzle is equipped with a ceramic or carbon liner for protecting the outer metal case surrounding the liner. Propellants which contain metals in their formulation may introduce problems because of the tendency of their exhaust gases to erode the throat of the exhaust nozzle. Considerable research and development effort is required for developing satisfactory temperature resisting materials for protecting the inert parts of solid propellant rocket motors.

Of importance is the fact that the heat transferred to the burning surface of a solid propellant grain by the hot combustion gases flowing past the surface does not penetrate far below that surface, because of the rapid rate with which the surface recedes. Consequently, the changes in temperature of the propellant grain due to the heat transfer need not be considered in internal ballistic studies.

Under transportation and short time storage conditions the temperature of the propellant grain in a solid propellant rocket motor will generally be different from that of the ambient atmosphere. The heat transfer from the atmosphere to the propellant takes place at a slow rate, and when the temperature difference is substantial, significant temperature gradients can arise in the grain that cause severe thermal stresses. If the grain is being cooled by the ambient temperature, assuming a case-bonded internal-burning grain, then the grain tries to pull away from the case and there are large tensile stresses at its inner and outer surfaces. (17, 18)

6-6. DESIGN CONCLUSIONS (1, 12)

The design details of a solid propellant rocket engine will depend upon the mission it must fulfill, the storage temperatures and temperature cycling it will encounter, and the conditions it will be subjected to under field handling conditions. By and large most of the requirements to be satisfied are of a practical nature and are not subject to an accurate analytical study. Once the specific propellant formulation has been decided upon, the designer has considerable latitude in selecting such parameters as the combustion pressure, burning

rate, grain configuration, and the design of the case.

The problems which must be solved in developing solid propellant motors are primarily those pertinent to obtaining precise thrust termination, accurate thrust vector control, and means for taking into account the temperature sensitivity of the propellant.

6-6.1. Selection of the Combustion Pressure.

For a rocket motor equipped with a conventional type of exhaust nozzle having fixed geometry, the following design criteria apply:

(a) The combustion pressure p_c should be at least 100 psia above the combustion limit (see Paragraph 6-4.2) corresponding to the lowest value of propellant temperature t_p which is to be encountered.

(b) The combustion pressure should be well below the pressure limit corresponding to the highest value of t_p to be encountered (see Paragraph 6-4.2). In general, higher combustion pressures are employed for short duration boost applications where a large but brief thrust is desired, and moderate combustion pressures for long duration applications where the weight of the inert parts of the rocket motor must be kept as light as possible.

(c) The combustion pressure depends upon the selection of the linear burning rate r_0 obtainable from the propellant formulation. Note that the relation between p_c and r_0 is exponential (see equation 6-2).

6-6.2. Estimation of Size and Weight of Propellant Grain.

The total weight of a solid propellant grain, denoted by W_p, depends upon the total impulse required for satisfying the requirements of the mission. If F denotes the thrust required (assumed to remain constant during the burning time τ_b) and I_s is the specific impulse of the propellant, then

$$W_p = F\tau_b/I_s \qquad (6\text{-}11)$$

Equation (6-11) gives the minimum weight of solid propellant for the required total impulse. That weight should be increased by 1 to 3 percent, depending upon the uniformity of the product and the closeness with which it meets the design specifications, to allow for slivers of the propellant that are not consumed. It cannot be overempha-

sized that the development and application of reliable process control procedures are as much a part of the development of a satisfactory solid propellant, as is the chemical research which enters into determining the most satisfactory propellant formulation.

If γ_p denotes the specific weight of the propellant, and V_p the volume of the grain, then

$$V_p = W_p/\gamma_p \qquad (6\text{-}12)$$

6-6.3. Determination of Grain Dimensions and Nozzle Throat Area.

The exact dimensions of the propellant grain depend upon the configuration which is selected: internal-burning star, rod and tube, etc. (13) In general, the shape of the grain must be such that its burning area S_p has the correct value for producing the required thrust throughout the burning period.

The throat area of the exhaust nozzle A_t may be determined from any one of the following three relationships. (1) Thus

$$A_t = S_p/K_n \qquad (6\text{-}13)$$

$$A_t = \dot{W}_p/C_w\,p_c \qquad (6\text{-}14)$$

$$A_t = F/C_w\,p_c \qquad (6\text{-}15)$$

where the weight flow coefficient C_w (see equation 3-17) is obtained from experimental data pertinent to the propellant.

The exit area for the nozzle depends on the expansion ratio for the exhaust nozzle (p_e/p_c) and the specific heat ratio k, for the combustion gases (see Chapter 4).

6-6.4. Effect of Grain Shape.

The thrust of a solid propellant rocket motor, like the combustion pressure, varies with the area of the burning surface S_p. Consequently, variation in the area of the burning surface can be utilized for programming the thrust as a function of the burning time. (14, 15, 16) The programming is accomplished by shaping the grain in such a manner that the desired amount of burning surface is provided at each instant during the burning period.

A grain designed for maintaining the area of the burning surface constant during the burning period produces a constant thrust throughout that period and is termed a neutral-burning grain. A grain which burns so that the thrust increases

with the burning time is said to be a progressive-burning grain, and one for which the thrust decreases with the burning time is called a regressive-burning grain.

With case-bonded, internal-burning, star-shaped, or cruciform grain, it is possible by proper arrangement of the geometric proportions between the number of points of the star, the angle between those points, and web thickness, to obtain either neutral, progressive, or regressive burning characteristics.

In addition to the aforementioned geometric type of control, the area of the burning surface can also be varied by employing inhibiting coatings so that certain areas of the grain are prevented from burning.

A third method of thrust program control which may be preferable for certain applications can be accomplished by constructing the grain from propellants having different burning rates.

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TABLE 1. MOLAR SPECIFIC HEATS AT CONSTANT PRESSURE FOR C-H-N-O COMPOUNDS

(C_p in cal/mol °K)

(Gordon, J. S., Wright Air Development Center, TR57-33, January 1957)

Temperature °K	°R	C (gas)	C (graphite)	CH4	CO	CO2	H	H2	H2O	N	N2	NO	NO2	N2O	NH3	O	O2	O3	OH
298.16	437	4.980	2.066	8.522	6.965	8.874	4.968	6.892	8.025		6.960	7.139	9.07	9.232	8.505	5.236	7.021	9.372	7.146
300	540	4.980	2.083	8.538	6.965	8.895	4.968	6.895	8.026		6.961	7.138	9.08	9.253	8.52	5.234	7.023	9.393	7.145
400	720	4.974	2.851	9.689	7.013	9.877	4.968	6.974	8.186		6.991	7.160	9.83	10.207	9.18	5.134	7.196	10.43	7.077
500	900	4.972	3.498	11.08	7.121	10.665	4.968	6.993	8.415		7.070	7.289	10.54	10.965	9.92	5.080	7.431	11.26	7.050
600	1080	4.971	4.03	12.49	7.276	11.310	4.968	7.008	8.676		7.196	7.468	11.14	11.590	10.65	5.049	7.670	11.86	7.054
700	1260	4.970	4.43	13.82	7.450	11.846	4.968	7.035	8.954		7.351	7.656	11.63	12.110	11.35	5.028	7.883	12.30	7.087
800	1440	4.969	4.75	15.05	7.624	12.292	4.968	7.078	9.245		7.513	7.833	12.02	12.452	12.11	5.015	8.063	12.62	7.149
900	1620	4.969	4.98	16.16	7.786	12.667	4.968	7.139	9.546		7.670	7.990	12.32	12.903	12.78	5.006	8.212	12.86	7.233
1000	1800	4.969	5.14	17.17	7.931	12.979	4.968	7.219	9.850		7.815	8.125	12.54	13.206	13.40	4.999	8.336	13.04	7.332
1100	1980	4.969	5.27	18.06	8.057	13.243	4.968	7.310	10.151		7.945	8.240	12.75	13.458	13.98	4.994	8.439	13.17	7.440
1200	2160	4.969	5.42	18.85	8.168	13.465	4.968	7.407	10.440		8.060	8.338	12.93	13.671	14.51	4.989	8.527	13.28	7.552
1300	2340	4.970	5.57	19.54	8.263	13.656	4.968	7.509	10.723		8.162	8.422	13.0	13.854	14.99	4.986	8.604	13.37	7.663
1400	2520	4.972	5.67	20.15	8.346	13.815	4.968	7.615	10.986		8.250	8.494	13.1	14.009	15.42	4.984	8.674	13.44	7.771
1500	2700	4.974	5.76	20.69	8.417	13.952	4.968	7.720	11.233		8.328	8.555	13.2	14.142	15.80	4.982	8.738	13.50	7.874
1600	2880	4.978	5.83	21.16	8.480	14.073	4.968	7.823	11.462		8.396	8.614	13.3		16.15	4.981	8.800	13.54	7.972
1700	3000	4.983	5.90	21.58	8.535	14.177	4.968	7.923	11.673		8.456	8.660	13.3		16.46	4.979	8.858	13.58	8.064
1800	3240	4.989	5.96	21.95	8.583	14.268	4.968	8.019	11.868		8.509	8.702	13.4		16.73	4.978	8.916	13.62	8.150
1900	3420	4.998	6.01	22.27	8.626	14.351	4.968	8.109	12.048		8.556	8.734	13.4		16.97	4.978	8.973	13.65	8.231
2000	3600	5.007	6.05	22.56	8.664	14.423	4.968	8.195	12.213		8.598	8.766	13.5		17.19	4.978	9.029	13.67	8.306
2100	3780	5.018	6.10	22.82	8.698	14.489	4.968	8.276	12.365	4.970	8.636	8.796			17.40	4.978	9.084	13.69	8.376
2200	3960	5.031	6.14	23.05	8.728	14.546	4.968	8.354	12.505	4.971	8.670	8.823			17.58	4.978	9.139	13.71	8.441
2300	4140	5.045	6.18	23.25	8.756	14.599	4.968	8.427	12.634	4.972	8.700	8.847			17.75	4.979	9.194	13.73	8.503
2400	4320	5.060	6.22	23.44	8.781	14.648	4.968	8.498	12.753	4.975	8.728	8.870			17.89	4.981	9.248	13.74	8.560
2500	4500	10.99	6.26	23.60	8.804	14.691	4.968	8.565	12.862	4.978	8.753	8.891			18.01	4.983	9.301	13.75	8.614
2600	4680	11.50	6.29	23.75	8.825	14.733	4.968	8.629	12.964	4.982	8.776	8.910			18.12	4.986	9.354	13.76	8.665
2700	4860	12.01	6.32	23.89	8.844	14.771	4.968	8.690	13.058	4.987	8.798	8.928			18.23	4.990	9.405	13.77	8.714
2800	5040	12.52	6.36	24.01	8.863	14.807	4.968	8.748	13.146	4.994	8.818	8.946			18.33	4.994	9.455	13.78	8.760
2900	5220	13.03	6.39	24.13	8.879	14.840	4.968	8.804	13.227	5.002	8.836	8.962			18.42	4.999	9.503	13.79	8.804
3000	5400	13.55	6.42	24.23	8.895	14.872	4.968	8.859	13.303	5.011	8.852	8.977			18.50	5.004	9.551	13.80	8.846
3100	5580	14.07	6.45	24.32	8.910	14.902	4.968	8.912	13.374	5.022	8.868	8.992			18.58	5.010	9.596	13.81	8.887
3200	5760	14.59	6.48	24.41	8.924	14.929	4.968	8.964	13.440	5.035	8.882	9.006				5.017	9.640	13.81	8.926
3300	5940	15.11	6.51	24.49	8.937	14.956	4.968	9.014	13.503	5.050	8.897	9.020				5.025	9.682	13.82	8.964
3400	6120	15.63	6.54	24.56	8.949	14.981	4.968	9.064	13.561	5.068	8.910	9.033				5.033	9.723	13.82	9.001
3500	6300	16.16	6.57	24.63	8.961	15.005	4.968	9.113	13.616	5.087	8.922	9.046				5.041	9.762	13.83	9.037
3600	6480	16.68	6.60	24.69	8.973	15.029	4.968	9.160	13.668	5.108	8.934	9.058				5.050	9.799	13.83	9.072
3700	6660	17.21	6.63	24.75	8.984	15.053	4.968	9.207	13.718	5.131	8.946	9.070				5.060	9.835	13.84	9.107
3800	6840	17.74	6.66	24.80	8.994	15.075	4.968	9.253	13.764	5.157	8.956	9.082				5.070	9.869	13.84	9.141
3900	7020	18.27	6.69	24.85	9.004	15.097	4.968	9.298	13.809	5.184	8.967	9.094				5.081	9.901	13.84	9.175
4000	7200	18.81	6.72	24.90	9.014	15.118	4.968	9.342	13.849	5.214	8.977	9.105				5.091	9.932	13.85	9.209
4100	7380	19.34		24.94	9.024	15.138	4.968	9.386	13.890	5.246	8.988	9.117				5.103	9.960	13.85	9.243
4200	7560	19.88		24.98	9.033	15.158	4.968	9.428	13.927	5.280	8.996	9.128				5.114	9.987	13.85	9.276
4300	7740	20.42		25.02	9.042	15.178	4.968	9.470	13.964	5.316	9.005	9.139				5.126	10.013	13.85	9.310
4400	7920	20.96		25.05	9.051	15.196	4.968	9.512	13.997	5.353	9.014	9.150				5.138	10.037	13.86	9.344
4500	8100	21.50		25.08	9.059	15.216	4.968	9.553	14.031	5.393	9.022	9.161				5.150	10.060	13.86	9.378
4600	8280	22.04			9.068	15.234	4.968	9.593	14.061	5.434	9.030	9.171				5.162	10.081		9.412
4700	8460	22.58			9.076	15.254	4.968	9.632	14.093	5.476	9.039	9.182				5.174	10.103		9.446
4800	8640	23.13			9.084	15.272	4.968	9.671	14.120	5.520	9.046	9.193				5.186	10.121		9.480
4900	8820	23.67			9.092	15.289	4.968	9.710	14.149	5.565	9.053	9.203				5.198	10.139		9.515
5000	9000	24.22			9.100	15.305	4.968	9.748	14.174	5.611	9.061	9.214				5.210	10.156		9.549
5100	9180	24.76			9.107	15.327	4.968	9.785	14.193	5.658	9.083	9.224				5.222	10.172		9.527
5200	9360	25.31			9.115	15.349	4.968	9.822	14.212	5.706	9.092	9.234				5.234	10.187		9.553
5300	9540	25.86			9.123	15.371	4.968	9.859	14.230	5.755	9.100	9.244				5.246	10.201		9.577
5400	9720	26.41			9.130	15.393	4.968	9.895	14.249	5.805	9.109	9.255				5.258	10.215		9.601
5500	9900	26.96			9.138	15.415	4.968	9.930	14.267	5.856	9.118	9.265				5.270	10.228		9.623
5600	10,080	27.51			9.145	15.437	4.968	9.965	14.286	5.902	9.127	9.274				5.282	10.239		9.644
5700	10,260	28.06			9.153	15.459	4.968	9.999	14.304	5.959	9.137	9.284				5.293	10.250		9.664
5800	10,440	28.61			9.160	15.481	4.968	10.034	14.322	6.011	9.146	9.294				5.305	10.261		9.683
5900	10,620	29.16			9.167	15.503	4.968	10.067	14.340	6.064	9.156	9.303				5.316	10.270		9.700
6000	10,800	29.71			9.175	15.525	4.968	10.100	14.358	6.118	9.166	9.313				5.327	10.279		9.716

APPENDIX

TABLES

TABLE 2. ENTHALPY OF C-H-N-O COMPOUNDS ABOVE t₀ = 298.16°K

(h in k cal/g-mol)

(Gordon, J. S., Wright Air Development Center, TR 57-33, January 1957)

Temperature °K	°R	C (gas)	C (graphite)	CH4	CO	CO2	H	H2	H2O	N	N2	NO	NO2	N2O	NH3	O	O2	O3	OH
298.16	437	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0
300	540	0.00916	0.0045	0.0157	0.013	0.017	0.0091	0.013	0.014		0.013	0.013	0.017	0.016	0.016	0.010	0.013	0.01726	0.013
400	720	.5069	.2512	0.9234	.7110	.941	.5059	0.7072	.823		.709	.726	.963	.991	.906	.528	.723	1.0102	.723
500	900	1.0042	0.5694	1.9616	1.4172	1.986	1.003	1.406	1.653		1.412	1.250	1.98	2.051	1.869	1.038	1.4541	2.0973	1.429
600	1080	1.5014	.9466	3.1414	2.1370	3.085	1.450	2.105	2.508		2.125	2.187	3.07	3.180	2.927	1.544	2.2094	3.2556	2.135
700	1260	1.9984	1.3703	4.4585	2.8730	4.244	1.996	2.808	3.389		2.852	2.942	4.21	4.366	4.029	2.049	2.9873	4.4656	2.840
800	1440	2.4954	1.8300	5.9035	3.6269	5.452	2.493	3.514	4.298		3.595	3.715	5.39	5.599	5.204	2.550	3.7849	5.7130	3.552
900	1620	2.9924	2.3179	7.4657	4.3977	6.700	2.990	4.224	5.238		4.354	4.506	6.61	6.872	6.448	3.501	4.5990	6.9879	4.271
1000	1800	3.4893	2.8234	9.1336	5.1837	7.983	3.487	4.942	6.208		5.129	5.312	7.85	8.178	7.759	3.551	5.4265	8.2834	5.000
1100	1980	3.9862	3.344	10.896	5.9827	9.293	3.984	5.669	7.208		5.917	6.040	9.13	9.511	9.121	4.051	6.265	9.5946	5.738
1200	2160	4.4832	3.878	12.742	6.7943	10.630	4.480	6.404	8.238		6.717	6.960	10.42	10.867	10.557	4.550	7.114	10.918	6.488
1300	2340	4.9802	4.428	14.663	7.6161	11.987	4.977	7.150	9.297		7.529	7.798	11.69	12.224	12.075	5.049	7.970	12.251	7.249
1400	2520	5.4773	4.990	16.648	8.4466	13.360	5.474	7.906	10.382		8.349	8.644	12.98	13.638	13.638	5.547	8.834	13.592	8.020
1500	2700	5.9746	5.572	18.692	9.2847	14.749	5.971	8.673	11.494		9.178	9.497	14.29	15.045	15.244	6.046	9.704	14.939	8.803
1600	2880	6.4722	6.149	20.79	10.129	16.150	6.468	9.450	12.627		10.014	10.356	15.63		16.872	6.544	10.582	16.292	9.595
1700	3060	6.9703	6.735	22.92	10.980	17.563	6.964	10.237	13.785		10.857	11.219	16.95		18.53	7.042	11.464	17.649	10.397
1800	3240	7.4690	7.330	25.10	11.836	18.985	7.461	11.035	14.962		11.705	12.087	18.30		20.19	7.540	12.353	19.009	11.208
1900	3420	7.9684	7.928	27.31	12.696	20.416	7.958	11.841	16.157		12.559	12.960	19.64		21.88	8.038	13.248	20.37	12.027
2000	3600	8.4686	8.528	29.55	13.561	21.855	8.455	12.656	17.372		13.417	13.835	20.99		23.58	8.535	14.148	21.74	12.854
2100	3780	8.9699	9.138	31.82	14.430	23.301	8.952	13.480	18.600	8.949	14.278	14.714			25.32	9.033	15.053	23.11	13.689
2200	3960	9.4724	9.748	34.12	15.301	24.753	9.448	14.311	19.843	9.449	15.144	15.595			27.04	9.531	15.965	24.48	14.530
2300	4140	9.9763	10.363	36.43	16.175	26.210	9.945	15.150	21.101	9.946	16.012	16.479			28.79	10.029	16.881	25.85	15.377
2400	4320	10.481	10.98	38.77	17.052	27.672	10.441	15.997	22.371	10.443	16.884	17.365			30.55	10.527	17.803	27.23	16.230
2500	4500	10.99	11.60	41.12	17.931	29.140	10.938	16.850	23.652	10.491	17.758	18.254			32.33	11.025	18.731	28.600	17.089
2600	4680	11.50	12.23	43.49	18.812	30.610	11.435	17.709	24.942	11.439	18.634	19.144			34.10	11.524	19.663	29.976	17.953
2700	4860	12.01	12.85	45.87	19.696	32.086	11.932	18.575	26.244	11.938	19.513	20.037			35.88	12.022	20.601	31.354	18.822
2800	5040	12.52	13.49	48.27	20.581	33.564	12.429	19.447	27.553	12.437	20.393	20.931			37.65	12.522	21.544	32.732	19.695
2900	5220	13.03	14.14	50.68	21.468	35.047	12.925	20.325	28.874	12.936	21.276	21.826			39.41	13.021	22.492	34.112	20.572
3000	5400	13.55	14.78	53.10	22.357	36.532	13.422	21.208	30.200	13.437	22.160	22.724			41.19	13.521	23.445	35.492	21.456
3100	5580	14.07	15.42	55.52	23.246	38.021	13.919	22.210	31.530	13.939	23.046	23.622			43.04	14.022	24.402	36.873	22.342
3200	5760	14.59	16.07	57.96	24.138	39.513	14.416	22.990	32.874	14.442	23.934	24.523				14.523	25.364	38.254	23.233
3300	5940	15.11	16.72	60.41	25.031	41.007	14.913	23.889	34.220	14.946	24.823	25.424				15.025	26.330	39.636	24.127
3400	6120	15.63	17.37	62.86	25.926	42.504	15.409	24.793	35.573	15.452	25.713	26.328				15.528	27.301	41.018	25.026
3500	6300	16.16	18.02	65.32	26.821	44.003	15.906	25.702	36.933	15.959	26.605	27.232				16.029	28.274	42.401	25.928
3600	6480	16.68	18.68	67.79	27.718	45.505	16.403	26.616	38.298	16.469	27.497	28.137				16.537	29.252	43.785	26.833
3700	6660	17.21	19.34	70.26	28.616	47.009	16.900	27.534	39.667	16.981	28.392	29.044				17.042	30.235	45.169	27.742
3800	6840	17.74	20.01	72.74	29.514	48.516	17.397	28.457	41.039	17.506	29.287	29.952				17.548	31.220	46.553	28.654
3900	7020	18.27	20.68	75.22	30.414	50.024	17.893	29.384	42.421	18.013	30.182	30.861				18.056	32.208	47.937	29.569
4000	7200	18.81	21.35	77.71	31.315	51.535	18.390	30.316	43.804	18.532	31.080	31.771				18.565	33.200	49.322	30.488
4100	7380	19.34	22.02*	80.20	32.219	53.048	18.887	31.253	45.191	19.055	31.979	32.682				19.074	34.194	50.708	31.410
4200	7560	19.88	22.70	82.70	33.121	54.563	19.384	32.193	46.579	19.582	32.880	33.595				19.585	35.192	52.093	32.335
4300	7740	20.42	23.39	85.20	34.025	56.079	19.881	33.138	47.975	20.111	33.781	34.508				20.097	36.192	53.479	33.264
4400	7920	20.96	24.07	87.70	34.929	57.598	20.377	34.087	49.372	20.645	34.683	35.422				20.610	37.194	54.865	34.195
4500	8100	21.50	24.77	90.21	35.835	59.119	20.874	35.041	50.775	21.182	35.592	36.338				21.125	38.199	56.251	35.129
4600	8280	22.04	25.46		36.741	60.641	21.371	35.998	52.179	21.724	36.496	37.254				21.640	39.206		36.067
4700	8460	22.58	26.16		37.648	62.165	21.868	36.959	53.587	22.269	37.400	38.171				22.157	40.215		37.007
4800	8640	23.13	26.86		38.556	63.692	22.365	37.924	54.997	22.819	38.306	39.090				22.675	41.227		37.950
4900	8820	23.67	27.57		39.465	65.220	22.861	38.884	56.411	23.373	39.212	40.004				23.194	42.240		38.896
5000	9000	24.22	28.28		40.374	66.749	23.358	39.866	57.827	23.932	40.119	40.923				23.715	43.255		39.845
5100	9180	24.76	28.99		41.285	68.309	23.855	40.843	59.180	24.495	41.037	41.845				24.237	44.272		40.797
5200	9360	25.31	29.70		42.196	69.870	24.352	41.823	60.535	25.063	41.935	42.768				24.758	45.289		41.751
5300	9540	25.86	30.42		43.108	71.434	24.849	42.808	61.892	25.637	42.845	43.692				25.280	46.310		42.707
5400	9720	26.41	31.15		44.021	73.001	25.345	43.795	63.251	26.216	43.755	44.617				25.817	47.330		43.666
5500	9900	26.96	31.88		44.934	74.569	25.842	44.787	64.611	26.799	44.667	45.543				26.339	48.353		44.627
5600	10,080	27.51	32.61		45.848	76.140	26.339	45.781	65.974	27.387	45.579	46.470				26.863	49.376		45.591
5700	10,260	28.06	33.34		46.763	77.713	26.836	46.780	67.338	27.980	46.492	47.398				27.390	50.400		46.566
5800	10,440	28.61	34.08		47.679	79.288	27.333	47.781	68.704	28.579	47.406	48.327				27.925	51.425		47.523
5900	10,620	29.16	34.82		48.595	80.865	27.829	48.788	70.072	29.182	48.321	49.256				28.450	52.448		48.493
6000	10,800	29.71	35.57		49.512	82.445	28.326	49.795	71.441	29.790	49.237	50.187				28.980	53.479		49.463

* Values of C (graphite) above 4000°K are measured from t₀ = 300°K.

TABLE 3. VALUES OF THE PARAMETER $\theta_t = (p_e/p_c)^{(k-1)/k}$

For $p_c/p_s = 1.0$ to 500.0 and for $k = 1.20$ to $k = 1.39$

p_c/p_s	p_s/p_c	$k=$ 1.20	1.21	1.22	1.23	1.24	1.25	1.26	1.27	1.28	1.29	1.30	1.31	1.32	1.33	1.34	1.35	1.36	1.37	1.38	1.39
1.0	1.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
2.0	0.5000	0.89090	0.88666	0.88250	0.87844	0.87445	0.87055	0.86673	0.86298	0.85931	0.85571	0.85218	0.84872	0.84533	0.84199	0.83873	0.83552	0.83237	0.82928	0.82624	0.82326
3.0	0.3333	0.83269	0.82641	0.82028	0.81430	0.80845	0.80274	0.79716	0.79171	0.78638	0.78116	0.77606	0.77107	0.76619	0.76141	0.75673	0.75215	0.74766	0.74326	0.73896	0.73474
4.0	0.2500	0.79370	0.78616	0.77881	0.77165	0.76467	0.75786	0.75122	0.74474	0.73841	0.73224	0.72621	0.72032	0.71457	0.70895	0.70346	0.69809	0.69284	0.68770	0.68268	0.67776
5.0	0.2000	0.76473	0.75630	0.74810	0.74012	0.73235	0.72478	0.71741	0.71023	0.70324	0.69641	0.68976	0.68328	0.67695	0.67077	0.66474	0.65885	0.65310	0.64748	0.64199	0.63663
6.0	0.1667	0.74184	0.73274	0.72390	0.71531	0.70695	0.69883	0.69092	0.68323	0.67574	0.66845	0.66134	0.65442	0.64768	0.64110	0.63469	0.62843	0.62233	0.61637	0.61056	0.60488
7.0	0.1429	0.72302	0.71340	0.70406	0.69498	0.68617	0.67761	0.66929	0.66120	0.65333	0.64568	0.63823	0.63098	0.62392	0.61704	0.61034	0.60381	0.59745	0.59124	0.58518	0.57928
8.0	0.1250	0.70711	0.69705	0.68730	0.67785	0.66867	0.65976	0.65110	0.64270	0.63453	0.62659	0.61887	0.61135	0.60405	0.59693	0.59001	0.58327	0.57670	0.57030	0.56406	0.55798
9.0	0.1111	0.69336	0.68295	0.67286	0.66308	0.65360	0.64439	0.63547	0.62680	0.61839	0.61021	0.60227	0.59455	0.58704	0.57974	0.57264	0.56572	0.55900	0.55244	0.54606	0.53984
10.0	0.1000	0.68129	0.67058	0.66020	0.65014	0.64040	0.63096	0.62180	0.61292	0.60430	0.59593	0.58780	0.57991	0.57224	0.56478	0.55753	0.55048	0.54362	0.53694	0.53044	0.52411
15.0	0.06667	0.63677	0.62501	0.61365	0.60267	0.59207	0.58181	0.57189	0.56230	0.55301	0.54401	0.53530	0.52685	0.51867	0.51073	0.50302	0.49555	0.48829	0.48125	0.47440	0.46775
20.0	0.05000	0.60696	0.59457	0.58263	0.57111	0.56000	0.54928	0.53893	0.52894	0.51928	0.50994	0.50091	0.49218	0.48373	0.47554	0.46762	0.45994	0.45249	0.44528	0.43827	0.43148
25.0	0.04000	0.58481	0.57198	0.55965	0.54777	0.53633	0.52531	0.51468	0.50443	0.49454	0.48499	0.47577	0.46686	0.45825	0.44993	0.44188	0.43408	0.42654	0.41923	0.41216	0.40530
30.0	0.03333	0.56730	0.55417	0.54155	0.52941	0.51773	0.50649	0.49567	0.48525	0.47520	0.46552	0.45617	0.44715	0.43844	0.43003	0.42190	0.41404	0.40644	0.39909	0.39197	0.38508
35.0	0.02857	0.55291	0.53954	0.52670	0.51437	0.50251	0.49112	0.48016	0.46961	0.45945	0.44966	0.44023	0.43113	0.42236	0.41389	0.40571	0.39782	0.39019	0.38282	0.37568	0.36878
40.0	0.02500	0.54074	0.52718	0.51417	0.50168	0.48969	0.47818	0.46711	0.45646	0.44622	0.43636	0.42687	0.41772	0.40891	0.40040	0.39220	0.38428	0.37664	0.36926	0.36212	0.35522
45.0	0.02222	0.53023	0.51651	0.50336	0.49075	0.47866	0.46704	0.45589	0.44517	0.43487	0.42496	0.41542	0.40624	0.39739	0.38887	0.38065	0.37273	0.36508	0.35770	0.35056	0.34368
50.0	0.02000	0.52100	0.50715	0.49389	0.48118	0.46899	0.45731	0.44609	0.43531	0.42496	0.41501	0.40544	0.39624	0.38737	0.37884	0.37061	0.36268	0.35504	0.34766	0.34054	0.33367
55.0	0.01818	0.51279	0.49883	0.48547	0.47268	0.46042	0.44867	0.43740	0.42658	0.41619	0.40621	0.39662	0.38740	0.37852	0.36998	0.36175	0.35383	0.34619	0.33882	0.33171	0.32486
60.0	0.01667	0.50541	0.49135	0.47791	0.46505	0.45273	0.44093	0.42961	0.41876	0.40834	0.39834	0.38874	0.37950	0.37062	0.36208	0.35385	0.34593	0.33831	0.33095	0.32386	0.31702
70.0	0.01429	0.49259	0.47838	0.46481	0.45184	0.43942	0.42754	0.41616	0.40526	0.39480	0.38478	0.37515	0.36591	0.35703	0.34849	0.34028	0.33238	0.32478	0.31746	0.31040	0.30360
80.0	0.01250	0.48175	0.46743	0.45376	0.44070	0.42821	0.41628	0.40486	0.39392	0.38344	0.37340	0.36377	0.35453	0.34566	0.33714	0.32895	0.32108	0.31350	0.30622	0.29920	0.29244
90.0	0.01111	0.47238	0.45797	0.44422	0.43110	0.41856	0.40658	0.39513	0.38418	0.37369	0.36364	0.35401	0.34478	0.33593	0.32743	0.31926	0.31142	0.30388	0.29663	0.28965	0.28294
100.0	0.01000	0.46416	0.44967	0.43586	0.42269	0.41011	0.39811	0.38664	0.37567	0.36517	0.35513	0.34551	0.33629	0.32746	0.31898	0.31084	0.30303	0.29552	0.28831	0.28137	0.27470
110.0	0.00909	0.45684	0.44229	0.42842	0.41521	0.40261	0.39058	0.37910	0.36812	0.35763	0.34759	0.33799	0.32879	0.31997	0.31152	0.30341	0.29562	0.28815	0.28097	0.27407	0.26744
120.0	0.00833	0.45027	0.43566	0.42176	0.40852	0.3959	0.38385	0.37236	0.36138	0.35089	0.34087	0.33127	0.32209	0.31329	0.30487	0.29679	0.28903	0.28160	0.27445	0.26759	0.26099
140.0	0.00714	0.43884	0.42416	0.41019	0.39690	0.38425	0.37219	0.36069	0.34973	0.33925	0.32925	0.31969	0.31055	0.30180	0.29342	0.28540	0.27771	0.27033	0.26326	0.25646	0.24994
160.0	0.00625	0.42919	0.41445	0.40044	0.38712	0.37445	0.36239	0.35090	0.33995	0.32950	0.31952	0.31000	0.30090	0.29219	0.28387	0.27590	0.26826	0.26095	0.25394	0.24721	0.24076
180.0	0.00556	0.42084	0.40605	0.39202	0.37868	0.36601	0.35395	0.34247	0.33153	0.32111	0.31117	0.30168	0.29262	0.28396	0.27568	0.26777	0.26019	0.25293	0.24598	0.23932	0.23292
200.0	0.00500	0.41352	0.39870	0.38465	0.37130	0.35863	0.34657	0.33511	0.32419	0.31380	0.30389	0.29444	0.28542	0.27681	0.26858	0.26071	0.25319	0.24598	0.23909	0.23248	0.22615
250.0	0.00400	0.39842	0.38356	0.36948	0.35613	0.34347	0.33145	0.32003	0.30917	0.29885	0.28902	0.27966	0.27074	0.26223	0.25411	0.24636	0.23895	0.23188	0.22510	0.21862	0.21242
300.0	0.00333	0.38649	0.37160	0.35752	0.34419	0.33155	0.31957	0.30821	0.29741	0.28716	0.27741	0.26813	0.25930	0.25089	0.24287	0.23522	0.22792	0.22094	0.21428	0.20791	0.20182
350.0	0.00286	0.37669	0.36180	0.34772	0.33441	0.32181	0.30987	0.29856	0.28783	0.27764	0.26796	0.25876	0.25001	0.24169	0.23376	0.22620	0.21899	0.21211	0.20555	0.19928	0.19328
400.0	0.00250	0.36841	0.35351	0.33945	0.32617	0.31360	0.30171	0.29045	0.27977	0.26965	0.26004	0.25091	0.24224	0.23399	0.22614	0.21866	0.21154	0.20475	0.19827	0.19208	0.18618
450.p	0.00222	0.36124	0.34635	0.33231	0.31906	0.30653	0.29468	0.28347	0.27285	0.26279	0.25324	0.24418	0.23558	0.22740	0.21962	0.21222	0.20517	0.19846	0.19206	0.18595	0.18012
500.0	0.00200	0.35496	0.34008	0.32606	0.31284	0.30034	0.28854	0.27738	0.26681	0.25680	0.24732	0.23832	0.22978	0.22167	0.21396	0.20663	0.19965	0.19301	0.18667	0.18064	0.17488

TABLE 4. VALUES OF THE PARAMETER $\sqrt{Z_t}$ AS A FUNCTION OF p_c/p_e

$$Z_t = 1 - \left(\frac{p_e}{p_c}\right)^{(k-1)/k} \quad (\text{where } p_e < p_c)$$

For $p_c/p_e = 1.0$ to 500.0 and for $k = 1.20$ to $k = 1.39$

p_c/p_e	p_e/p_c	$k=$ 1.20	1.21	1.22	1.23	1.24	1.25	1.26	1.27	1.28	1.29	1.30	1.31	1.32	1.33	1.34	1.35	1.36	1.37	1.38	1.39
1.0	1.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2.0	0.5000	0.33030	0.33666	0.34278	0.34866	0.35432	0.35979	0.36506	0.37016	0.37509	0.37986	0.38447	0.38895	0.39329	0.39750	0.40159	0.40556	0.40943	0.41318	0.41684	0.42040
3.0	0.3333	0.40904	0.41664	0.42393	0.43093	0.43766	0.44414	0.45038	0.45639	0.46220	0.46780	0.47322	0.47847	0.48354	0.48846	0.49323	0.49785	0.50234	0.50669	0.51092	0.51504
4.0	0.2500	0.45420	0.46243	0.47031	0.47786	0.48511	0.49208	0.49878	0.50523	0.51145	0.51746	0.52325	0.52884	0.53425	0.53949	0.54456	0.54946	0.55422	0.55884	0.56331	0.56766
5.0	0.2000	0.48505	p.49366	0.50190	0.50979	0.51735	0.52461	0.53159	0.53830	0.54476	0.55099	0.55699	0.56278	0.56838	0.57379	0.57902	0.58408	0.58898	0.59373	0.59834	0.60280
6.0	0.1667	0.50810	0.51697	0.52545	0.53357	0.54134	0.54879	0.55595	0.56282	0.56944	0.57581	0.58194	0.58786	0.59357	0.59908	0.60441	0.60957	0.61455	0.61938	0.62405	0.62858
7.0	0.1429	0.52629	0.53535	0.54401	0.55228	0.56020	0.56779	0.57507	0.58206	0.58878	0.59525	0.60147	0.60747	0.61326	0.61884	0.62423	0.62944	0.63447	0.63934	0.64406	0.64863
8.0	0·1250	0 54119	0.55041	0.55919	0 56759	0.57562	0.58331	0.59068	0.59775	0.60454	0.61108	0.61736	0.62341	0.62925	0.63488	0.64031	0.64555	0.65062	0.65552	0.66026	0.66485
9.0	0.1111	0.55375	0.56307	0.57196	0.58045	0.58856	0.59633	0.60376	0.61090	0.61775	0.62433	0.63066	0.63675	0.64262	0.64827	0.65373	0.65900	0.66408	0.66900	0.67375	0.67835
10.0	0.1000	0 56454	0.57396	0.58293	0.59149	0.59966	0.60749	0.61498	0.62216	0.62905	0.63567	0.64203	0.64814	0.65404	0.65971	0.66518	0.67046	0.67556	0.68048	0.68524	0.68984
15.0	0.06667	0.60268	0.61237	0.62157	0.63034	0.63870	0.64668	0.65430	0.66159	0.66858	0.67527	0.68169	0.68786	0.69378	0.69948	0.70497	0.71025	0.71534	0.72024	0.72498	0.72955
20.0	0.05000	0.62693	0.63673	0.64604	0.65490	0.66332	0.67136	0.67902	0.68634	0.69334	0.70004	0.70646	0.71262	0.71852	0.72419	0.72965	0.73489	0.73994	0.74480	0.74948	0.75400
25.0	0.04000	0.64436	0.65423	0.66359	0.67248	0.68093	0.68898	0.69665	0.70397	0.71096	0.71764	0.72404	0.73016	0.73603	0.74167	0.74708	0.75228	0.75727	0.76208	0.76671	0.77117
30.0	0 03333	0.65780	0.66771	0.67709	0.68600	0.69445	0.70250	0.71016	0.71746	0.72443	0.73108	0.73745	0.74354	0.74937	0.75497	0.76033	0.76548	0.77043	0.77518	0.77976	0.78417
35.0	0.02857	0.66865	0.67857	0.68797	0.69687	0.70533	0.71336	0.72100	0.72828	0.73522	0.74185	0.74818	0.75423	0.76003	0.76558	0.77090	0.77600	0.78090	0.78561	0.79014	0.79449
40.0	0.02500	0.67768	0.68762	0.69702	0.70592	0.71436	0.72237	0.73000	0.73725	0.74416	0.75076	0.75705	0.76307	0.76883	0.77434	0.77962	0.78468	0.78953	0.79419	0.79867	0.80298
45.0	0.02222	0.68540	0.69533	0.70473	0.71361	0.72204	0.73004	0.73764	0.74487	0.75175	0.75831	0.76458	0.77056	0.77628	0.78175	0.78699	0.79201	0.79682	0.80144	0.80588	0.81014
50.0	0.02000	0.69210	0.70203	0.71141	0.72029	0.72870	0.73668	0.74425	0.75146	0.75831	0.76484	0.77107	0.77702	0.78270	0.78814	0.79334	0.79832	0.80310	0.80768	0.81207	0.81629
55.0	0.01818	0.69801	0.70793	0.71731	0.72617	0.73456	0.74252	0.75007	0.75725	0.76407	0.77058	0.77678	0.78269	0.78834	0.79374	0.79890	0.80385	0.80859	0.81313	0.81749	0.82167
60.0	0.01667	0.70327	0.71319	0 72256	0 73140	0 73978	0 74771	0.75524	0.76239	0.76919	0.77567	0.78183	0.78772	0.79333	0.79870	0.80383	0.80874	0.81345	0.81795	0.82228	0.82642
70.0	0.01429	0.71233	0.72223	0.73157	0.74038	0.74872	0.75661	0.76409	0.77120	0.77794	0.78436	0.79048	0.79630	0.80186	0.80716	0.81223	0.81708	0.82172	0.82616	0.83042	0.83450
80.0	0.01250	0.71990	0.72978	0.73908	0.74787	0.75617	0.76402	0.77146	0.77851	0.78521	0.79158	0.79764	0.80341	0.80891	0.81416	0.81918	0.82397	0.82855	0.83294	0 83714	0.84116
90.0	0.01111	0.72637	0.73623	0.74551	0.75426	0.76252	0.77033	0.77773	0.78474	0.79140	0.79772	0 80373	0.80945	0.81491	0.82011	0.82507	0.82981	0.83434	0.83867	0.84282	0.84680
100.0	0.01000	0.73201	0.74184	0.75109	0.75981	0.76804	0.77582	0.78318	0.79015	0.79676	0.80304	0.80900	0.81468	0.82009	0.82524	0.83016	0.83485	0.83933	0.84362	0.84772	0.85165
110.0	0.00909	0.73700	0.74680	0.75603	0.76471	0.77291	0.78065	0.78797	0.79491	0.80148	0.80772	0.81364	0.81928	0.82464	0.82975	0.83462	0.83927	0.84371	0.84795	0.85201	0.85590
120.0	0.00833	0.74144	0.75122	0.76042	0.76908	0.77724	0.78495	0.79224	0.79914	0.80567	0.81187	0.81776	0.82335	0.82868	0.83375	0.83858	0.84319	0.84759	0.85179	0.85581	0.85966
140.0	0.00714	0.74911	0.75884	0.76799	0.77659	0.78470	0.79235	0.79957	0.80640	0.81286	0.81899	0.82481	0.83033	0.83559	0.84058	0.84534	0.84988	0.85421	0.85834	0.86229	0.86606
160.0	0.00625	0.75552	0.76521	0.77431	0.78286	0.79092	0.79850	0.80567	0.81244	0.81884	0.82491	0.83066	0.83612	0.84131	0.84625	0.85094	0.85542	0.85968	0.86375	0.86763	0.87135
180.0	0.00556	0.76103	0.77068	0.77973	0.78824	0.79624	0.80378	0.81088	0.81760	0.82395	0.82996	0.83566	0.84106	0.84619	0.85107	0.85571	0.86012	0.86433	0.86834	0.87217	0.87583
200.0	0.00500	0.76582	0.77543	0.78444	0.79290	0.80086	0.80835	0.81541	0.82207	0.82837	0.83433	0.83998	0.84533	0.85041	0.85523	0.85982	0.86418	0.86834	0.87230	0.87608	0.87969
250.0	0.00400	0.77561	0.78514	0.79406	0.80242	0.81027	0.81765	0.82460	0.83116	0.83735	0.84320	0.84873	0.85397	0.85894	0.86365	0.86812	0.87238	0.87643	0.88028	0.88395	0.88746
300.0	0.00333	0.78327	0.79271	0.80155	0.80982	0.81759	0.82488	0.83174	0.83820	0.84430	0.85005	0.85549	0.86064	0.86551	0.87013	0.87452	0.87868	0.88264	0.88641	0.88999	0.89341
350.0	0 00286	0.78950	0.79888	0.80764	0 81584	0.82352	0 83074	0.83752	0.84390	0 84992	0.85559	0.86095	0.86602	0.87081	0.87535	0.87966	0.88375	0.88763	0.89132	0.89483	0.89817
400.0	0.00250	0.79473	0.80404	0.81274	0.82087	0.82849	0.83564	0.84235	0.84866	0.85461	0.86021	0.86550	0.87049	0.87522	0.87969	0.88393	0.88795	0.89177	0.89539	0.89884	0.90212
450.0	0.00222	0.79923	0.80848	0.81712	0.82519	0.83275	0.83983	0.84648	0.85273	0.85861	0.86415	0.86938	0.87431	0.87898	0.88339	0.88757	0.89153	0.89529	0.89886	0.90225	0.90547
500.0	0 00200	0.80315	0.81235	0.82094	0.82895	0.83645	0.84348	0.85007	0.85626	0.86209	0.86757	0.87274	0.87762	0.88223	0.88659	0.89071	0.89462	0.89833	0.90185	0.90519	0.90836

TABLE 5. FUNCTIONS OF THE SPECIFIC HEAT RATIO k

k	$\frac{1}{k}$	$\sqrt{k}$	$\sqrt{1/k}$	$\frac{1}{\sqrt{k}}$	$\frac{2}{k}$	$\frac{2}{\sqrt{k}}$	k^2	$\frac{1}{k-1}$	$\sqrt{\frac{1}{k-1}}$	$\sqrt{k-1}$	$\frac{1}{k+1}$	$\sqrt{\frac{1}{k+1}}$	$\sqrt{k+1}$	$\frac{2}{k-1}$	$\frac{k}{k-1}$	$\frac{2}{k+1}$	$\frac{k}{k+1}$	$\sqrt{\frac{k}{k+1}}$	$\sqrt{\frac{k}{k-1}}$
1.10	0.90909	1.0488	0.95346	0.95346	1.8181	1.9069	1.2100	10.000	3.1622	0.31623	0.47619	0.69007	1.4491	20.000	11.000	0.95238	0.52381	0.72375	3.3166
1.11	0.90090	1.0535	0.94916	0.94916	1.8018	1.8983	1.2321	9.0909	3.0151	0.33166	0.47393	0.68843	1.4525	18.181	10.090	0.94787	0.52607	0.72530	3.1766
1.12	0.89286	1.0583	0.94491	0.94491	1.7857	1.8898	1.2544	8.3333	2.8867	0.34641	0.47170	0.68680	1.4560	16.666	9.333	0.94340	0.52830	0.72684	3.0550
1.13	0.88496	1.0630	0.94072	0.94072	1.7699	1.8814	1.2769	7.6923	2.7735	0.36056	0.46948	0.68519	1.4594	15.384	8.6923	0.93897	0.53052	0.72837	2.9482
1.14	0.87719	1.0677	0.93659	0.93659	1.7543	1.8731	1.2996	7.1428	2.6726	0.37417	0.46729	0.68359	1.4628	14.285	8.1428	0.93458	0.53271	0.72987	2.8535
1.15	0.86957	1.0723	0.93250	0.93251	1.7391	1.8650	1.3225	6.6666	2.5819	0.38730	0.46512	0.68199	1.4662	13.333	7.6666	0.93023	0.53488	0.73136	2.7688
1.16	0.86207	1.0770	0.92848	0.92848	1.7241	1.8569	1.3456	6.2500	2.5000	0.40000	0.46296	0.68041	1.4696	12.500	7.2500	0.92593	0.53704	0.73283	2.6925
1.17	0.85470	1.0816	0.92450	0.92450	1.7094	1.8490	1.3689	5.8823	2.4253	0.41231	0.46083	0.67884	1.4730	11.764	6.8823	0.92166	0.53917	0.73428	2.6234
1.18	0.84746	1.0862	0.92057	0.92057	1.6949	1.8411	1.3924	5.5555	2.3570	0.42426	0.45872	0.67729	1.4764	11.111	6.5555	0.91743	0.54128	0.73572	2.5603
1.19	0.84034	1.0908	0.91670	0.91670	1.6806	1.8334	1.4161	5.2631	2.2941	0.43589	0.45662	0.67574	1.4798	10.526	6.2631	0.91324	0.54338	0.73714	2.5026
1.20	0.83333	1.0954	0.91287	0.91287	1.6666	1.8257	1.4400	5.0000	2.2360	0.44721	0.45455	0.67420	1.4832	10.000	6.0000	0.90909	0.54545	0.73855	2.4494
1.21	0.82645	1.1000	0.90909	0.90909	1.6528	1.8181	1.4641	4.7619	2.1821	0.45826	0.45249	0.67267	1.4866	9.5238	5.7619	0.90498	0.54751	0.73994	2.4004
1.22	0.81967	1.1045	0.90536	0.90536	1.6393	1.8107	1.4884	4.5454	2.1320	0.46904	0.45045	0.67116	1.4899	9.0909	5.5454	0.90090	0.54955	0.74132	2.3548
1.23	0.81301	1.1090	0.90167	0.90167	1.6260	1.8033	1.5129	4.3478	2.0851	0.47958	0.44843	0.66965	1.4933	8.6956	5.3478	0.89686	0.55157	0.74268	2.3125
1.24	0.80645	1.1135	0.89803	0.89803	1.6129	1.7960	1.5376	4.1666	2.0412	0.48990	0.44643	0.66815	1.4966	8.3333	5.1666	0.89286	0.55357	0.74402	2.2730
1.25	0.80000	1.1180	0.89443	0.89443	1.6000	1.7888	1.5625	4.0000	2.0000	0.50000	0.44444	0.66667	1.5000	8.0000	5.0000	0.88889	0.55556	0.74536	2.2360
1.26	0.79365	1.1225	0.89087	0.89087	1.5873	1.7817	1.5876	3.8461	1.9611	0.50990	0.44248	0.66519	1.5033	7.6923	4.8461	0.88496	0.55752	0.74667	2.2014
1.27	0.78740	1.1269	0.88736	0.88736	1.5748	1.7747	1.6129	3.7037	1.9245	0.51962	0.44053	0.66372	1.5066	7.4074	4.7037	0.88106	0.55947	0.74798	2.1688
1.28	0.78125	1.1313	0.88388	0.88388	1.5625	1.7677	1.6384	3.5714	1.8898	0.52915	0.43860	0.66227	1.5099	7.1428	4.5714	0.87719	0.56140	0.74927	2.1380
1.29	0.77519	1.1357	0.88045	0.88045	1.5503	1.7609	1.6641	3.4482	1.8569	0.53852	0.43668	0.66082	1.5132	6.8965	4.4482	0.87336	0.56332	0.75055	2.1090
1.30	0.76923	1.1401	0.87706	0.87706	1.5384	1.7541	1.6900	3.3333	1.8257	0.54772	0.43478	0.65938	1.5165	6.6666	4.3333	0.86957	0.56522	0.75181	2.0816
1.31	0.76336	1.1445	0.87370	0.87370	1.5267	1.7474	1.7161	3.2258	1.7960	0.55678	0.43290	0.65795	1.5198	6.4516	4.2258	0.86580	0.56710	0.75306	2.0556
1.32	0.75758	1.1489	0.87039	0.87039	1.5151	1.7407	1.7424	3.1250	1.7677	0.56569	0.43103	0.65653	1.5231	6.2500	4.1250	0.86207	0.56897	0.75430	2.0310
1.33	0.75188	1.1532	0.86711	0.86711	1.5037	1.7342	1.7689	3.0303	1.7407	0.57446	0.42918	0.65512	1.5264	6.0606	4.0303	0.85837	0.57082	0.75552	2.0075
1.34	0.74627	1.1575	0.86387	0.86387	1.4925	1.7277	1.7956	2.941	1.7149	0.58310	0.42735	0.65372	1.5297	5.8823	3.9411	0.85470	0.57265	0.75674	1.9852
1.35	0.74074	1.1619	0.86066	0.86066	1.4814	1.7213	1.8225	2.8571	1.6903	0.59161	0.42553	0.65233	1.5329	5.7142	3.8571	0.85106	0.57447	0.75794	1.9639
1.36	0.73529	1.1661	0.85749	0.85749	1.4705	1.7149	1.8496	2.7777	1.6666	0.60000	0.42373	0.65094	1.5362	5.5555	3.7777	0.84746	0.57627	0.75913	1.9436
1.37	0.72993	1.1704	0.85436	0.85436	1.4598	1.7087	1.8769	2.7027	1.6439	0.60828	0.42194	0.64957	1.5394	5.4054	3.7027	0.84388	0.57806	0.76030	1.9242
1.38	0.72464	1.1747	0.85126	0.85126	1.4492	1.7025	1.9044	2.6315	1.6222	0.61644	0.42017	0.64820	1.5427	5.2631	3.6315	0.84034	0.57983	0.76147	1.9056
1.39	0.71942	1.1789	0.84819	0.84819	1.4388	1.6963	1.9321	2.5641	1.6012	0.62450	0.41841	0.64685	1.5459	5.1282	3.5641	0.83682	0.58159	0.76262	1.8878
1.40	0.71429	1.1832	0.84515	0.84515	1.4285	1.6903	1.9600	2.5000	1.5811	0.63246	0.41667	0.64550	1.5491	5.0000	3.5000	0.83333	0.58333	0.76376	1.8708
1.41	0.70922	1.1874	0.84215	0.84215	1.4184	1.6843	1.9881	2.4390	1.5617	0.64031	0.41494	0.64416	1.5524	4.8780	3.4390	0.82988	0.58506	0.76489	1.8544
1.42	0.70423	1.1916	0.83918	0.83918	1.4084	1.6783	2.0164	2.3809	1.5430	0.64807	0.41322	0.64282	1.5556	4.7619	3.3809	0.82645	0.58678	0.76601	1.8387
1.43	0.69930	1.1958	0.83624	0.83624	1.3986	1.6724	2.0449	2.3255	1.5249	0.65574	0.41152	0.64150	1.5588	4.6511	3.3255	0.82305	0.58848	0.76712	1.8236
1.44	0.69444	1.2000	0.83333	0.83333	1.3888	1.6666	2.0736	2.2727	1.5075	0.66332	0.40984	0.64018	1.5620	4.5454	3.2727	0.81967	0.59016	0.76822	1.8090
1.45	0.68966	1.2041	0.83045	0.83046	1.3793	1.6609	2.1025	2.2222	1.4907	0.67082	0.40816	0.63888	1.5652	4.4444	3.2222	0.81633	0.59184	0.76931	1.7950
1.46	0.68493	1.2083	0.82761	0.82761	1.3698	1.6552	2.1316	2.1739	1.4744	0.67823	0.40650	0.63758	1.5684	4.3478	3.1739	0.81301	0.59350	0.77039	1.7815
1.47	0.68027	1.2124	0.82479	0.82479	1.3605	1.6495	2.1609	2.1276	1.4586	0.68557	0.40486	0.63628	1.5716	4.2553	3.1276	0.80972	0.59514	0.77145	1.7685
1.48	0.67568	1.2165	0.82199	0.82200	1.3513	1.6439	2.1904	2.0833	1.4433	0.69282	0.40323	0.63500	1.5748	4.1666	3.0833	0.80615	0.59677	0.77251	1.7559
1.49	0.67114	1.2206	0.81923	0.81923	1.3422	1.6384	2.2201	2.0408	1.4285	0.70000	0.40161	0.63372	1.5779	4.0816	3.0408	0.80321	0.59839	0.77356	1.7437
1.50	0.66667	1.2247	0.81650	0.81650	1.3333	1.6329	2.2500	2.0000	1.4142	0.70711	0.40000	0.63246	1.5811	4.0000	3.0000	0.80000	0.60000	0.77460	1.7320
1.51	0.66225	1.2288	0.81379	0.81379	1.3245	1.6275	2.2801	1.9607	1.4002	0.71414	0.39841	0.63119	1.5843	3.9215	2.9607	0.79681	0.60159	0.77562	1.7206
1.52	0.65789	1.2328	0.81111	0.81111	1.3157	1.6222	2.3104	1.9230	1.3867	0.72111	0.39683	0.62994	1.5874	3.8461	2.9230	0.79365	0.60317	0.77664	1.7097
1.53	0.65359	1.2369	0.80845	0.80845	1.3071	1.6169	2.3409	1.8867	1.3736	0.7281	0.39526	0.62869	1.5906	3.7735	2.8867	0.79051	0.60474	0.77765	1.6990
1.54	0.64935	1.2409	0.80582	0.80582	1.2987	1.6116	2.3716	1.8518	1.3608	0.73485	0.39370	0.62746	1.5937	3.7037	2.8518	0.78740	0.60630	0.77865	1.6887
1.55	0.64516	1.2449	0.80322	0.80322	1.2903	1.6064	2.4025	1.8181	1.3484	0.74162	0.39216	0.62622	1.5968	3.6363	2.8181	0.78431	0.60784	0.77964	1.6787
1.56	0.64103	1.2490	0.80064	0.80064	1.2820	1.6012	2.4336	1.7857	1.3363	0.74833	0.39073	0.62500	1.6000	3.5714	2.7857	0.78125	0.60938	0.78062	1.6690
1.57	0.63694	1.2530	0.79809	0.79809	1.2738	1.5961	2.4649	1.7543	1.3245	0.75498	0.38911	0.62378	1.6031	3.5087	2.7543	0.77821	0.61089	0.78160	1.6596
1.58	0.63291	1.2569	0.79556	0.79556	1.2658	1.5911	2.4964	1.7241	1.3130	0.76158	0.38760	0.62257	1.6062	3.4482	2.7241	0.77519	0.61240	0.78256	1.6505
1.59	0.62893	1.2609	0.79305	0.79305	1.2578	1.5861	2.5281	1.6949	1.3018	0.76811	0.38610	0.62137	1.6093	3.3898	2.6949	0.77220	0.61390	0.78352	1.6416
1.60	0.62500	1.2649	0.79057	0.79057	1.2500	1.5811	2.5600	1.6666	1.2909	0.77460	0.38462	0.62017	1.6124	3.3333	2.6666	0.76923	0.61538	0.78446	1.6329
1.61	0.62112	1.2688	0.78811	0.78811	1.2422	1.5762	2.5921	1.6393	1.2803	0.78102	0.38314	0.61898	1.6155	3.2786	2.6393	0.76628	0.61686	0.78540	1.6246
1.62	0.61728	1.2727	0.78567	0.78567	1.2345	1.5713	2.6244	1.6129	1.2700	0.78740	0.38168	0.61780	1.6186	3.2258	2.6129	0.76336	0.61832	0.78633	1.6164
1.63	0.61350	1.2767	0.78326	0.78326	1.2269	1.5665	2.6569	1.5873	1.2598	0.79373	0.38023	0.61663	1.6217	3.1746	2.5873	0.76046	0.61977	0.78726	1.6085
1.64	0.60976	1.2806	0.78087	0.78087	1.2195	1.5617	2.6896	1.5625	1.2500	0.80000	0.37879	0.61546	1.6248	3.1250	2.5625	0.75758	0.62121	0.78817	1.6007
1.65	0.60606	1.2845	0.77850	0.77850	1.2121	1.5570	2.7225	1.5384	1.2403	0.80623	0.37736	0.61429	1.6278	3.0769	2.5384	0.75472	0.62264	0.78908	1.5932
1.66	0.60241	1.2884	0.77615	0.77615	1.2048	1.5523	2.7556	1.5151	1.2309	0.81240	0.37594	0.61314	1.6309	3.0303	2.5151	0.75188	0.62406	0.78997	1.5859
1.67	0.59880	1.2922	0.77382	0.77382	1.1976	1.5476	2.7889	1.4925	1.2216	0.81854	0.37453	0.61199	1.6340	2.9850	2.4925	0.74906	0.62547	0.79087	1.5787
1.68	0.59524	1.2961	0.77152	0.77152	1.1904	1.5430	2.8224	1.4705	1.2126	0.82462	0.37313	0.61085	1.6370	2.9411	2.4705	0.74627	0.62687	0.79175	1.5718
1.69	0.59172	1.3000	0.76923	0.76923	1.1834	1.5384	2.8561	1.4492	1.2038	0.83066	0.37175	0.60971	1.6401	2.8985	2.4492	0.74349	0.62825	0.79262	1.5650

TABLE 5. (Continued)

k	$\frac{k-1}{k}$	$\frac{k+1}{k}$	$\frac{k-1}{k+1}$	$\frac{k+1}{k-1}$	$\sqrt{\frac{k-1}{k}}$	$\sqrt{\frac{k+1}{k}}$	$\sqrt{\frac{k-1}{k+1}}$	$\sqrt{\frac{k+1}{k-1}}$	$\sqrt{\frac{2}{k+1}}$	$\sqrt{\frac{2}{k-1}}$	$\left(\frac{k+1}{2}\right)^{\frac{1}{k-1}}$	$\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}$	$\left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}$	$\left(\frac{2}{k+1}\right)^{\frac{k+1}{2(k-1)}}$	$\frac{2gk}{k-1}$	$\sqrt{\frac{2gk}{k-1}}$	Ω	$\left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}$	$\Omega\sqrt{k}$
1.10	0.09091	1.9090	0.04762	21.000	0.30151	1.3817	0.21822	4.5825	0.97590	4.4721	1.6288	0.61392	0.58468	0.59912	707.94	26.607	0.62836	0.35895	0.65903
1.11	0.09910	1.9009	0.05213	19.181	0.31480	1.3787	0.22832	4.3797	0.97358	4.2640	1.6269	0.61464	0.58260	0.59840	649.43	25.483	0.63045	0.35808	0.66423
1.12	0.10714	1.8928	0.05660	17.666	0.32733	1.3758	0.23791	4.2031	0.97129	4.0824	1.6250	0.61536	0.58053	0.59769	600.67	24.508	0.63253	0.35723	0.66941
1.13	0.11504	1.8849	0.06103	16.384	0.33918	1.3729	0.24705	4.0477	0.96900	3.9223	1.6232	0.61606	0.57846	0.59697	559.42	23.652	0.63458	0.35637	0.67457
1.14	0.12281	1.8771	0.06542	15.285	0.35044	1.3701	0.25577	3.9096	0.96674	3.7796	1.6213	0.61677	0.57642	0.59625	524.06	22.892	0.63662	0.35552	0.67973
1.15	0.13043	1.8695	0.06977	14.333	0.36116	1.3673	0.26413	3.7859	0.96449	3.6514	1.6195	0.61747	0.57439	0.59554	493.41	22.212	0.63864	0.35467	0.68487
1.16	0.13793	1.8620	0.07407	13.500	0.37139	1.3645	0.27217	3.6742	0.96225	3.5355	1.6176	0.61816	0.57237	0.59482	466.60	21.600	0.64064	0.35381	0.68999
1.17	0.14550	1.8547	0.07834	12.764	0.38118	1.3618	0.27989	3.5727	0.96003	3.4299	1.6158	0.61886	0.57037	0.59412	442.93	21.045	0.64264	0.35298	0.69512
1.18	0.15254	1.8474	0.08257	12.111	0.39057	1.3592	0.28735	3.4801	0.95783	3.3333	1.6140	0.61955	0.56840	0.59342	421.90	20.540	0.64462	0.35215	0.70024
1.19	0.15966	1.8403	0.08676	11.526	0.39958	1.3565	0.29455	3.3950	0.95564	3.2444	1.6122	0.62024	0.56643	0.59272	403.08	20.076	0.64658	0.35132	0.70534
1.20	0.16667	1.8333	0.09091	11.000	0.40825	1.3540	0.30151	3.3166	0.95346	3.1622	1.6105	0.62092	0.56447	0.59202	386.15	19.650	0.64853	0.35049	0.71043
1.21	0.17355	1.8264	0.09502	10.523	0.41660	1.3514	0.30826	3.2440	0.95130	3.0860	1.6087	0.62161	0.56254	0.59134	370.82	19.256	0.65047	0.34968	0.71551
1.22	0.18033	1.8196	0.09910	10.090	0.42465	1.3489	0.31480	3.1766	0.94916	3.0151	1.6069	0.62228	0.56061	0.59064	356.89	18.891	0.65239	0.34886	0.72058
1.23	0.18699	1.8130	0.10314	9.6956	0.43242	1.3464	0.32115	3.1137	0.94703	2.9488	1.6052	0.62296	0.55870	0.58996	344.18	18.552	0.65429	0.34805	0.72564
1.24	0.19355	1.8064	0.10714	9.3333	0.43994	1.3440	0.32733	3.0550	0.94491	2.8867	1.6035	0.62363	0.55681	0.58927	332.52	18.235	0.65619	0.34724	0.73070
1.25	0.20000	1.8000	0.11111	9.0000	0.44721	1.3416	0.33333	3.0000	0.94281	2.8284	1.6018	0.62430	0.55493	0.58859	321.79	17.938	0.65807	0.34644	0.73574
1.26	0.20635	1.7936	0.11504	8.6923	0.45426	1.3392	0.33918	2.9482	0.94072	2.7735	1.6001	0.62496	0.55306	0.58792	311.89	17.660	0.65993	0.34564	0.74077
1.27	0.21260	1.7874	0.11894	8.4074	0.46108	1.3369	0.34488	2.8995	0.93865	2.7216	1.5984	0.62562	0.55121	0.58724	302.72	17.398	0.66178	0.34485	0.74579
1.28	0.21875	1.7812	0.12281	8.1428	0.46771	1.3346	0.35044	2.8535	0.93659	2.6726	1.5967	0.62628	0.54937	0.58656	294.21	17.152	0.66362	0.34406	0.75080
1.29	0.22481	1.7751	0.12664	7.8965	0.47414	1.3323	0.35586	2.8100	0.93454	2.6261	1.5950	0.62694	0.54755	0.58590	286.28	16.919	0.66545	0.34328	0.75581
1.30	0.23077	1.7692	0.13043	7.6666	0.48038	1.3301	0.36116	2.7688	0.93250	2.5819	1.5933	0.62759	0.54573	0.58523	278.88	16.699	0.66726	0.34249	0.76079
1.31	0.23664	1.7633	0.13420	7.4516	0.48646	1.3279	0.36633	2.7297	0.93048	2.5400	1.5917	0.62824	0.54393	0.58456	271.96	16.491	0.66906	0.34171	0.76578
1.32	0.24242	1.7575	0.13793	7.2500	0.49237	1.3257	0.37139	2.6925	0.92848	2.5000	1.5901	0.62888	0.54214	0.58390	265.48	16.293	0.67085	0.34094	0.77075
1.33	0.24812	1.7518	0.14163	7.0606	0.49812	1.3235	0.37634	2.6571	0.92648	2.4618	1.5885	0.62953	0.54036	0.58324	259.38	16.105	0.67263	0.34017	0.77571
1.34	0.25373	1.7462	0.14530	6.8823	0.50372	1.3214	0.38118	2.6234	0.92450	2.4253	1.5868	0.63016	0.53860	0.58259	253.65	15.926	0.67439	0.33941	0.78066
1.35	0.25926	1.7407	0.14894	6.7142	0.50917	1.3193	0.38592	2.5911	0.92253	2.3904	1.5852	0.63080	0.53685	0.58193	248.24	15.755	0.67615	0.33865	0.78561
1.36	0.26471	1.7352	0.15254	6.5555	0.51449	1.3173	0.39057	2.5603	0.92057	2.3570	1.5837	0.63143	0.53511	0.58128	243.13	15.592	0.67789	0.33789	0.79054
1.37	0.27007	1.7299	0.15612	6.4054	0.51968	1.3152	0.39512	2.5308	0.91863	2.3249	1.5821	0.63207	0.53339	0.58064	238.30	15.436	0.67962	0.33714	0.79547
1.38	0.27536	1.7246	0.15966	6.2631	0.52475	1.3132	0.39958	2.5026	0.91670	2.2941	1.5805	0.63269	0.53167	0.57999	233.72	15.287	0.68133	0.33639	0.80038
1.39	0.28058	1.7194	0.16318	6.1282	0.52969	1.3112	0.40395	2.4755	0.91478	2.2645	1.5789	0.63332	0.52997	0.57934	229.38	15.145	0.68304	0.33564	0.80529
1.40	0.28571	1.7142	0.16667	6.0000	0.53452	1.3093	0.40825	2.4494	0.91287	2.2360	1.5774	0.63394	0.52828	0.57870	225.25	15.008	0.68473	0.33490	0.81019
1.41	0.29078	1.7092	0.17012	5.8780	0.53924	1.3073	0.41246	2.4244	0.91097	2.2086	1.5759	0.63456	0.52660	0.57807	221.33	14.877	0.68642	0.33416	0.81507
1.42	0.29577	1.7042	0.17355	5.7619	0.54385	1.3054	0.41660	2.4004	0.90909	2.1821	1.5743	0.63517	0.52494	0.57743	217.59	14.750	0.68809	0.33343	0.81995
1.43	0.30070	1.6993	0.17695	5.6511	0.54836	1.3035	0.42066	2.3772	0.90722	2.1566	1.5728	0.63579	0.52328	0.57680	214.03	14.629	0.68975	0.33270	0.82482
1.44	0.30556	1.6944	0.18033	5.5454	0.55277	1.3017	0.42465	2.3548	0.90536	2.1320	1.5713	0.63640	0.52164	0.57617	210.63	14.513	0.69140	0.33198	0.82968
1.45	0.31034	1.6896	0.18367	5.4444	0.55709	1.2998	0.42857	2.3333	0.90351	2.1081	1.5698	0.63701	0.52000	0.57554	207.38	14.400	0.69304	0.33124	0.83453
1.46	0.31507	1.6849	0.18699	5.3478	0.56131	1.2980	0.43242	2.3125	0.90167	2.0851	1.5683	0.63761	0.51838	0.57491	204.27	14.292	0.69467	0.33052	0.83937
1.47	0.31973	1.6802	0.19028	5.2553	0.56544	1.2962	0.43621	2.2924	0.89984	2.0628	1.5668	0.63821	0.51677	0.57429	201.29	14.187	0.69629	0.32981	0.84420
1.48	0.32432	1.6756	0.19355	5.1666	0.56949	1.2944	0.43994	2.2730	0.89803	2.0412	1.5654	0.63881	0.51517	0.57367	198.44	14.086	0.69790	0.32909	0.84903
1.49	0.32886	1.6711	0.19679	5.0816	0.57346	1.2927	0.44361	2.2542	0.89622	2.0203	1.5639	0.63941	0.51358	0.57305	195.70	13.989	0.69950	0.32839	0.85384
1.50	0.33333	1.6666	0.20000	5.0000	0.57735	1.2909	0.44721	2.2360	0.89443	2.0000	1.5625	0.64000	0.51200	0.57243	193.07	13.894	0.70108	0.32768	0.85865
1.51	0.33775	1.6622	0.20319	4.9215	0.58116	1.2892	0.45076	2.2184	0.89264	1.9802	1.5610	0.64059	0.51043	0.57182	190.55	13.803	0.70266	0.32698	0.86345
1.52	0.34211	1.6578	0.20635	4.8461	0.58490	1.2875	0.45426	2.2014	0.89087	1.9611	1.5596	0.64118	0.50887	0.57121	188.12	13.715	0.70423	0.32628	0.86823
1.53	0.34641	1.6535	0.20949	4.7735	0.58856	1.2859	0.45770	2.1848	0.88911	1.9425	1.5582	0.64176	0.50732	0.57060	185.79	13.630	0.70579	0.32558	0.87301
1.54	0.35065	1.6493	0.21260	4.7037	0.59316	1.2842	0.46108	2.1688	0.88736	1.9245	1.5567	0.64235	0.50579	0.56999	183.54	13.547	0.70734	0.32489	0.87779
1.55	0.35484	1.6451	0.21569	4.6363	0.59568	1.2826	0.46442	2.1532	0.88561	1.9069	1.5553	0.64293	0.50426	0.56939	181.37	13.467	0.70888	0.32420	0.88255
1.56	0.35897	1.6410	0.21875	4.5714	0.59914	1.2810	0.46771	2.1380	0.88388	1.8898	1.5539	0.64351	0.50274	0.56879	179.28	13.389	0.71041	0.32352	0.88730
1.57	0.36306	1.6369	0.22179	4.5087	0.60254	1.2794	0.47094	2.1233	0.88216	1.8731	1.5525	0.64408	0.50123	0.56819	177.27	13.314	0.71193	0.32284	0.89205
1.58	0.36709	1.6329	0.22481	4.4482	0.60588	1.2778	0.47414	2.1090	0.88045	1.8569	1.5512	0.64466	0.49973	0.56759	175.32	13.240	0.71345	0.32216	0.89679
1.59	0.37107	1.6289	0.22780	4.3898	0.60915	1.2763	0.47728	2.0951	0.87875	1.8411	1.5498	0.64523	0.49824	0.56699	173.44	13.169	0.71495	0.32148	0.90152
1.60	0.37500	1.6250	0.23077	4.3333	0.61237	1.2747	0.48038	2.0816	0.87706	1.8257	1.5484	0.64580	0.49677	0.56640	171.62	13.100	0.71645	0.32081	0.90624
1.61	0.37888	1.6211	0.23372	4.2786	0.61553	1.2732	0.48344	2.0685	0.87538	1.8107	1.5471	0.64636	0.49530	0.56581	169.86	13.033	0.71793	0.32014	0.91095
1.62	0.38272	1.6172	0.23664	4.2258	0.61864	1.2717	0.48646	2.0556	0.87370	1.7960	1.5457	0.64693	0.49384	0.56522	168.16	12.967	0.71941	0.31947	0.91566
1.63	0.38650	1.6135	0.23954	4.1746	0.62169	1.2702	0.48943	2.0431	0.87204	1.7817	1.5444	0.64749	0.49239	0.56464	166.51	12.903	0.72088	0.31881	0.92035
1.64	0.39024	1.6097	0.24242	4.1250	0.62469	1.2687	0.49237	2.0310	0.87039	1.7677	1.5431	0.64804	0.49094	0.56405	164.92	12.842	0.72233	0.31815	0.92504
1.65	0.39394	1.6060	0.24528	4.0769	0.62765	1.2673	0.49526	2.0191	0.86874	1.7541	1.5417	0.64860	0.48951	0.56347	163.37	12.781	0.72379	0.31749	0.92972
1.66	0.39759	1.6024	0.24812	4.0303	0.63055	1.2658	0.49812	2.0075	0.86711	1.7407	1.5404	0.64915	0.48808	0.56289	161.87	12.722	0.72523	0.31684	0.93439
1.67	0.40120	1.5988	0.25094	3.9850	0.63340	1.2644	0.50094	1.9962	0.86548	1.7277	1.5391	0.64970	0.48667	0.56231	160.41	12.665	0.72666	0.31619	0.93905
1.68	0.40476	1.5952	0.25373	3.9411	0.63621	1.2630	0.50372	1.9852	0.86387	1.7149	1.5378	0.65025	0.48526	0.56173	159.00	12.609	0.72809	0.31554	0.94371
1.69	0.40828	1.5917	0.25651	3.8985	0.63897	1.2616	0.50646	1.9744	0.86226	1.7025	1.5365	0.65080	0.48387	0.56116	157.63	12.555	0.72951	0.31490	0.94836

TABLE 6. ENTHALPIES OF FORMATION OF FUELS AT 300°K

$(\Delta H_f^o/\text{in k cal/g-mol})$

(Martinez, J. S. and Elverum, G. W., Jet Propulsion Laboratory, California Institute
of Technology, Tech. Memo. No. 20-121, December 6, 1955)

Fuel	Formula	Heat of Formation		
		Gas	Liquid	Solid
Ammonia	NH_3	11.04*	16.52*	17.97*
Aniline	$C_6H_5NH_2$		−6.11	
Acetylene	C_2H_2	−54.193	−50.6	
Benzene	C_6H_6	−19.726	−11.718*	
1-Butylene	C_4H_8	−0.254		
n-Butane	C_4H_{10}	29.847	34.882	
1-Butyne (ethylacetylene)	C_4H_6	−39.68		
2-Butyne (dimethyacetylene)	C_4H_6	−35.355		
Beryllium hydride	BeH	−78.1*		
Boron (atom)	B	−97.2*		
Boron	B_2	−124.5*		0
Cyanogen	C_2N_2	−73.60*		
n-Decane	$C_{10}H_{22}$	59.74		
Dimethylamine	C_2H_7N	6.6*		
Dimethylaminodiborane	$(CH_3)_2NB_2H_5$	61.6		
Diborane	B_2H_6	−6.7±0.5		
Diethylenetriamine	$C_4H_{13}N_3$	3.15	15.40	
Dimethylhydrazine (Unsymmetrical)	$C_2N_2H_8$	−19.636	−11.27	
Ethylene oxide	C_2H_4O	12.19*	18.44	
Ethanol	C_2H_6O	56.27	67.2	
Ethyl nitrite	$C_2H_5O_2N$	24.8*		
Ethyl nitrate	$C_2H_5O_3N$		44.3*	
Furfural	$C_5H_4O_2$		46.6	
Furfuryl alcohol	$C_5H_6O_2$		66.05	
Guanidine nitrate	$CH_6O_3N_4$	91.1*		
n-Hexane	C_6H_{14}	40.01	47.52*	
n-Heptane	C_7H_{16}	44.94	53.63*	
Hydrogen	H_2	0	1.92	
Hydrogen cyanide	HCN	−31.2*		
Hydrazine hydrate	$N_2H_4H_2O$		10.3	
Hydrazine	N_2H_4	−22.70	−12.0	
JP-4	H/C=1.93		0.421	
			(K cal/g)	
Lithium	Li_2	−38.437		0
Lithium hydride	LiH	−30.7*		21.61*
Methyl alcohol	CH_3OH	48.08*	57.04*	
Methyl hydrazine	$(CH_3)N_2H_3$	−22.758	−13.11	
Nitromethane	CH_3O_2N		21.28*	
Nitroguanidine	$CH_4O_2N_4$	22.14*		
n-Octane	C_8H_{18}	49.88	59.795	
1-Octene	C_8H_{16}	19.87		
Pentaborane	B_5H_9	−15.0*	−7.8*	
Propene (propylene)	C_3H_6	−4.858		
Propane	C_3H_8	24.848	28.443	
Propyne (methylactylene)	C_3H_4	−44.309		
Propyl nitrate	$C_3H_7NO_3$	43.2	52.8	
Tetranitromethane	CHO_6N_3	18.6*		
Trimethyl boron	$B(CH_3)_3$	31.4*		

* Values of ΔH_f^o at 298°K.

PROPULSION AND PROPELLANTS

TABLE 7. ENTHALPIES OF FORMATION FOR OXIDIZERS AT 300°K

(ΔH_f^o in k cal/g-mol)

(Martinez, J. S. and Elverum, G. W., Jet Propulsion Laboratory, California Institute of Technology, Tech. Memo. No. 20-121, December 6, 1955)

Oxidizer	Formula	Enthalpy of Formation		
		Gas	Liquid	Solid
Ammonium nitrate	NH_4NO_3			87.27*
Ammonium perchlorate	NH_4ClO_4			69.42*
Boron trichloride	BCl_3		94.5*	
Boron trifluoride	BF_3		265.4*	
Boron tribromide			44.6*	
Chlorine trifluoride	ClF_3	38.0	44.5	
Fluorine	F_2	0		
Fluorine monoxide	F_2O	−7.60		
Hydrogen peroxide	H_2O_2	33.74	44.84	47.36*
Nitrogen tetroxide	N_2O_4	−2.30	6.80	
Nitrogen trifluoride	NF_3	27.2*	31.2−129	
Nitric acid	HNO_3	31.92	41.35	
Oxygen	O_2	0	3.08−183	
Ozone	O_3	−34.00	−30.3	
Perchlorylfluoride	ClO_3F	2.56	7.3	
Potassium perchlorate	$KClO_4$		103.6*	
Tetranitromethane	$C(NO_2)_4$		−8.8* or −22	
Red fuming nitric acid	14% NO_2 1% H_2O		45.3	
Stabilized fuming nitric acid (HNO_3 + 0.2315 NO_2 + 0.1955 H_2O + 0.019 H_4) Avg mol wt 75.94	14% NO_2 2.5% H_2O 0.5% HF		51.5	

* Values of ΔH_f^o at 298°K.

TABLE 8. ENTHALPIES OF FORMATION FOR REACTION PRODUCTS AT 300°K

(ΔH_f^o in k cal/g-mol)

(Martinez, J. S. and Elverum, G. W., Jet Propulsion Laboratory, California Institute of Technology, Tech. Memo. No. 20-121, December 6, 1955)

Reaction Product	Formula	Enthalpy of Formation			Remarks
		Gas	Liquid	Solid	
Aluminum oxide	Al_2O_3			399.09	(a)
Aluminum hydroxide	$Al(OH)_3$			304.2	amorphous (a)
Ammonium fluoride	NH_4F			111.6	(a)
Ammonium chloride	NH_4Cl			75.38	(a)
Beryllium oxide	BeO	−11.8		145.3	(a)
Beryllium chloride	$BeCl_2$			122.3	(a)
Boric acid	H_3BO_3			260±3.5	
Boron nitride	BN	−90.6		32.1	(a)
Boron fluoride	BF	17.4			
Boron chloride	BCl	−25.6			
Boron monoxide	BO	5.3			
Boron trioxide	B_2O_3	223.2		302±3	
Carbon dioxide	CO_2	94.052			
Carbon monoxide	CO	26.413			
Carbon tetrafluoride	CF_4	231			
Carbon (graphite)	C			0	
Carbon (gas)	C	−171.698			
Chlorine (atom)	Cl	−28.943			
Cyanogen chloride	$CNCl$	−34.5			
Chlorine monofluoride	ClF	11.898 or 13.256			

TABLE 8. (Continued)

Reaction Product	Formula	Enthalpy of Formation			Remarks
		Gas	Liquid	Solid	
Fluorine (atom)	F	−18.906			
Hydroxyl	OH	−10.063			
Hydrogen (atom)	H	−52.092			
Hydrogen chloride	HCl	22.063			(a)
Hydrogen fluoride	HF	64.20			(a)
Hexa hydrogen fluorine	$(HF)_6$	426			(a)
Hydrogen sulfide	H_2S	4.815			(a)
Lithium	Li	−37.07		0.00	(a)
Lithium hydroxide	LiOH			116.45	(a)
Lithium	Li_2	−50.461			
Lithium oxide	Li_2O			142.4	(a)
Lithium chloride	LiCl	53		97.70	(a)
Lithium fluoride	LiF			146.3	(a)
Lithium oxychloride			91.6		(a)
Lithium nitride	Li_3N			47.2	(a)
Lithium peroxide	Li_2O_2			159	(a)
Nitrogen	N_2	0			
Nitrogen (atom)	N	−112.5			
Oxygen	O_2	0			
Oxygen (atomic)	O	−59.162			
Potassium chloride	KCl	51.60		104.175	(a)
Potassium oxide	K_2O			86.4	(a)
Sodium oxide	NaO_2			61.9	(a)
Sodium oxide	Na_2O			99.4	(a)
Sodium peroxide	Na_2O_2			120.6	(a)
Sodium hydroxide	NaOH			101.99	(a)
Sulfur	S	−53.25			(a)
Sulfur	S_2	−29.86			
Sulfur dioxide	SO_2	70.96			
Sulfur trioxide	SO_3	94.45			
Tetrabromomethane	CBr_4	−12			
Tetrachloromethane	CCl_4	25.5			
Tetrafluoromethane	CF_4	231±3			
Water	H_2O	57.802	68.317	69.753	
Zinc oxide	ZnO			83.17	
Zirconium oxide	ZrO_2			258.2	

(a) Values of ΔH_f^o at 298°K.

General Reference
 (b) Rossini, F. D., et al, Selected Values of Properties of Hydrocarbons, NBS 500, November 1947.

TABLE 9. EQUILIBRIUM CONSTANTS AS FUNCTIONS OF TEMPERATURE FOR C-H-N-O COMPOUNDS

(Gordon, J. S., Wright Air Development Center, TR57-33, January 1957)

(Martinez, J. S. and Elverum, G. W., Jet Propulsion Laboratory, California Institute of Technology, Tech. Memo. No. 20-121, December 6, 1955)

Temperature °K	°R	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8	K_9	K_{10}	K_{11}	K_{12}
298.16	436.68	9.614×10^{-6}	5.855×10^{-56}	8.05×10^{-81}	4.41×10^{-81}	2.49×10^{-36}	2.54×10^{-47}			834			
300	540	1.063×10^{-5}	1.332×10^{-55}	2.67×10^{-80}	1.48×10^{-80}	4.26×10^{-36}	5.068×10^{-47}	1.228×10^{-158}	4.973×10^{24}	741.5	5.757×10^{44}	8.133×10^{23}	0.8113×10^{-15}
400	720	6.457×10^{-4}	4.026×10^{-41}	3.30×10^{-59}	3.19×10^{-59}	1.35×10^{-26}	1.248×10^{-34}	1.233×10^{-117}	4.287×10^{15}	6.557	2.621×10^{32}	8.277×10^{104}	$.7499\times10^{-11}$
500	900	7.279×10^{-3}	2.095×10^{-32}	1.69×10^{-46}	2.23×10^{-46}	7.00×10^{-21}	3.485×10^{-27}	5.345×10^{-93}	1.216×10^{10}	3.393×10^{-1}	1.059×10^{25}	1.843×10^{83}	0.1604×10^{-8}
600	1080	0.0354	1.408×10^{-26}	5.4×10^{-38}	8.66×10^{-38}	4.65×10^{-17}	3.348×10^{-22}	1.490×10^{-76}	2.126×10^{6}	4.396×10^{-2}	1.222×10^{20}	6.427×10^{68}	$.5979\times10^{-7}$
700	1260	0.1060	2.108×10^{-22}	6.81×10^{-32}	1.24×10^{-31}	2.54×10^{-14}	1.248×10^{-18}	8.581×10^{-65}	3.971×10^{3}	9.804×10^{-3}	3.630×10^{16}	2.958×10^{58}	$.7988\times10^{-6}$
800	1440	.2360	2.901×10^{-19}	2.65×10^{-27}	5.23×10^{-27}	2.90×10^{-12}	6.053×10^{-16}	5.798×10^{-56}	3.439×10	3.098×10^{-3}	8.232×10^{13}	5.151×10^{50}	$.5596\times10^{-5}$
900	1620	.4340	8.096×10^{-17}	1.01×10^{-23}	2.12×10^{-23}	1.17×10^{-10}	7.510×10^{-14}	4.347×10^{-49}	0.788	1.247×10^{-3}	7.254×10^{11}	4.707×10^{44}	$.2545\times10^{-4}$
1000	1800	0.6958	7.56×10^{-15}	7.53×10^{-21}	1.65×10^{-20}	2.27×10^{-9}	3.579×10^{-12}	1.392×10^{-43}	3.932×10^{-2}	5.95×10^{-4}	1.654×10^{10}	6.893×10^{39}	0.8547×10^{-4}
1100	1980	1.010	3.02×10^{-13}	1.72×10^{-18}	3.89×10^{-18}	2.59×10^{-8}	8.513×10^{-11}	4.491×10^{-39}	3.311×10^{-3}	3.22×10^{-4}	7.532×10^{8}	7.598×10^{35}	2.302×10^{-4}
1200	2160	1.368	6.65×10^{-12}	1.60×10^{-16}	3.72×10^{-16}	1.97×10^{-7}	1.188×10^{-9}	2.589×10^{-35}	4.280×10^{-4}	1.94×10^{-4}	5.762×10^{7}	3.809×10^{33}	5.255×10^{-4}
1300	2340	1.757	9.13×10^{-11}	7.46×10^{-15}	1.77×10^{-14}	1.11×10^{-6}	1.114×10^{-8}	3.964×10^{-32}	7.366×10^{-5}	1.25×10^{-4}	6.571×10^{6}	6.127×10^{29}	1.056×10^{-3}
1400	2520	2.160	8.66×10^{-10}	2.03×10^{-13}	4.88×10^{-13}	4.86×10^{-6}	7.598×10^{-8}	2.140×10^{-29}	1.631×10^{-5}	8.61×10^{-5}	1.025×10^{6}	2.463×10^{27}	1.920×10^{-3}
1500	2700	2.572	6.09×10^{-9}	3.56×10^{-12}	8.67×10^{-12}	1.76×10^{-5}	4.016×10^{-7}	5.012×10^{-27}	4.441×10^{-6}	6.21×10^{-5}	2.054×10^{5}	2.061×10^{25}	3.225×10^{-3}
1600	2880	2.990	3.37×10^{-8}	4.38×10^{-11}	1.08×10^{-10}	5.43×10^{-5}	1.725×10^{-6}	5.957×10^{-26}		4.66×10^{-5}	5.046×10^{4}	3.131×10^{23}	5.076×10^{-3}
1700	3060	3.395	1.52×10^{-7}	4.02×10^{-10}	1.00×10^{-9}	1.47×10^{-4}	6.249×10^{-6}	4.046×10^{-23}		3.62×10^{-5}	1.465×10^{4}	7.768×10^{21}	7.572×10^{-3}
1800	3240	3.793	5.84×10^{-7}	2.90×10^{-9}	7.26×10^{-9}	3.57×10^{-4}	1.963×10^{-5}	1.724×10^{-21}		2.89×10^{-5}	4.890×10^{3}	2.902×10^{20}	1.081×10^{-2}
1900	3420	4.417	1.94×10^{-6}	1.70×10^{-8}	4.28×10^{-8}	7.926×10^{-4}	5.468×10^{-5}	4.957×10^{-20}		2.37×10^{-5}	1.835×10^{3}	1.530×10^{19}	1.487×10^{-2}
2000	3600	4.553	5.74×10^{-6}	8.34×10^{-8}	2.12×10^{-7}	0.001624	1.375×10^{-4}	1.020×10^{-18}		1.98×10^{-5}	7.609×10^{2}	1.082×10^{18}	1.982×10^{-2}
2100	3780	4.890	1.53×10^{-5}	3.53×10^{-7}	9.01×10^{-7}	.003111	3.169×10^{-4}	1.577×10^{-17}		1.69×10^{-5}	3.436×10^{2}	9.832×10^{16}	2.504×10^{-2}
2200	3960	5.218	3.735×10^{-5}	1.312×10^{-6}	3.364×10^{-6}	.005621	6.770×10^{-4}	1.902×10^{-16}		1.46×10^{-5}	1.670×10^{2}	1.110×10^{16}	3.239×10^{-2}
2300	4140	5.532	8.429×10^{-5}	4.348×10^{-6}	1.120×10^{-5}	.009660	1.354×10^{-3}	1.849×10^{-15}		1.28×10^{-5}	8.654×10	1.514×10^{15}	4.021×10^{-2}
2400	4320	5.823	1.778×10^{-4}	1.306×10^{-5}	3.378×10^{-5}	.01587	2.556×10^{-3}	1.489×10^{-14}		1.13×10^{-5}	4.742×10	2.436×10^{14}	4.901×10^{-2}
2500	4500	6.096	3.539×10^{-4}	3.595×10^{-5}	9.332×10^{-5}	0.02509	4.596×10^{-3}	1.016×10^{-13}			27.29	4.533×10^{13}	0.0588
2600	4680	6.358	6.676×10^{-4}	9.154×10^{-5}	2.385×10^{-4}	.03829	7.881×10^{-3}	5.983×10^{-13}			16.41	9.592×10^{12}	.0695
2700	4860	6.598	1.201×10^{-3}	2.178×10^{-4}	5.690×10^{-4}	.05669	0.01300	3.093×10^{-12}			10.25	2.276×10^{12}	.0812
2800	5040	6.827	2.074×10^{-3}	4.870×10^{-4}	1.276×10^{-3}	.08162	.02067	1.423×10^{-11}			6.630	5.981×10^{11}	.0938
2900	5220	7.022	3.450×10^{-3}	1.031×10^{-3}	2.709×10^{-3}	.1146	.03185	5.899×10^{-11}			4.422	1.723×10^{11}	.1073
3000	5400	7.226	5.534×10^{-3}	2.071×10^{-3}	5.460×10^{-3}	0.1575	0.04762	2.226×10^{-10}			3.032	5.387×10^{10}	0.1216
3100	5580	7.414	8.633×10^{-3}	3.988×10^{-3}	0.01054	.2121	.06946	7.717×10^{-10}			2.132	1.815×10^{10}	.1366
3200	5760	7.577	0.01309	7.381×10^{-3}	.01954	.2803	.09895	2.478×10^{-9}			1.534	6.542×10^{9}	.1524
3300	5940	7.725	.01936	0.01315	.03488	.3643	.1379	7.418×10^{-9}			1.126	2.507×10^{9}	.1689
3400	6120	7.871	.02799	.02270	.06024	.4662	.1886	2.084×10^{-8}			0.8424	1.016×10^{9}	.1860
3500	6300	8.011	0.03957	0.03784	0.1007	0.5888	0.2532	5.524×10^{-8}			0.6411	4.332×10^{8}	0.2036
3600	6480	8.132	.05495	.06146	.1638	.7340	.3344	1.388×10^{-7}			.4956	1.936×10^{8}	.2218
3700	6660	8.254	.07487	.09722	.2595	.9041	.4351	3.320×10^{-7}			.3887	9.034×10^{7}	.2403
3800	6840	8.349	.1005	.1505	.4017	1.102	.5587	7.591×10^{-7}			.3090	4.385×10^{7}	.2593
3900	7020	8.438	.1330	.2278	.6082	1.328	.7081	1.663×10^{-6}			.2486	2.208×10^{7}	.2786
4000	7200	8.523	0.1731	0.3372	0.9008	1.588	0.8861	3.532×10^{-6}			0.2023	1.150×10^{7}	0.2993
4100	7380	8.609	.2229	.4899	1.311	1.882	1.097	7.149×10^{-6}			.1664	6.180×10^{6}	.3185
4200	7560	8.679	.2834	.7004	1.873	2.213	1.346	1.406×10^{-5}			.1382	3.419×10^{6}	.3386
4300	7740	8.760	.3560	.9814	2.629	2.583	1.634	2.680×10^{-5}			.1158	1.944×10^{6}	.3589
4400	7920	8.809	.4427	1.357	3.639	2.993	1.966	4.962×10^{-5}			0.098	1.133×10^{6}	.3794
4500	8100	8.852	0.5462	1.856	4.970	3.444	2.348	8.941×10^{-5}		1.01×10^{-5}	0.0826	6.764×10^{5}	0.4000
4600	8280	8.904	.6670	2.499	6.692	3.942	2.782	1.570×10^{-4}		9.1×10^{-6}	.0708	4.127×10^{5}	.4207
4700	8460	8.952	.8073	3.323	8.896	4.485	3.271	2.694×10^{-4}		8.27×10^{-6}	.0611	2.571×10^{5}	.4415
4800	8640	8.992	.9694	4.363	11.69	5.078	3.822	4.518×10^{-4}		7.56×10^{-6}	.0531	1.633×10^{5}	.4623
4900	8820	9.024	1.156	5.675	15.19	5.717	4.437	7.422×10^{-4}		6.96×10^{-6}	.0461	1.057×10^{5}	.4833
5000	9000	9.048	1.370	7.318	19.56	6.407	5.125	1.196×10^{-3}		6.44×10^{-6}	0.0408	6.961×10^{4}	0.5049
5100	9180	9.070	1.605	9.420	24.89	7.145	5.861	1.891×10^{-3}			.0359	4.628×10^{4}	.5228
5200	9360	9.089	1.876	11.84	31.43	7.937	6.690	2.941×10^{-3}			.0320	3.151×10^{4}	.5453
5300	9540	9.095	2.181	14.83	39.37	8.780	7.598	4.499×10^{-3}			.0286	2.171×10^{4}	.5664
5400	9720	9.098	2.523	18.44	48.91	9.675	8.590	6.778×10^{-3}			.0256	1.516×10^{4}	.5875

TABLE 9. (Continued)

Temperature °K	°R	K_1	K_2	K_3	K_4	K_5	K_6	K_8	K_7	K_9	K_{10}	K_{11}	K_{12}
5500	9900	0.099	2.904	22.76	60.31	10.62	9.669	0.01007			0.0230	1.073×10^4	0.6087
5600	10,080	0.097	3.328	27.91	73.84	11.62	10.84	.01475			.0208	7.682×10^3	.6299
5700	10,260	0.092	3.797	34.00	89.82	12.68	12.10	.02133			.0189	5.566	.6512
5800	10,440	9.083	4.316	41.17	108.6	13.78	13.45	.03046			.0172	4.078	.6726
5900	10,620	9.071	4.889	49.58	130.5	14.93	14.86	.04301			.0157	3.019	.6943
6000	10,800	9.055	5.519	59.39	155.9	16.14	16.62	0.06004			0.0143	2.258×10^3	0.7161

$$K_1 = \frac{(CO)(H_2O)}{(CO_2)(H_2)};$$
$$K_2 = \frac{(NO)(H_2)}{(N_2)^{1/2}(H_2O)};$$
$$K_3 = \frac{(H_2)^2(O_2)}{(H_2O)^2};$$
$$K_4 = \frac{(H_2)(O)}{(H_2O)};$$
$$K_5 = \frac{(H)}{(H_2)^{1/2}};$$

$$K_6 = \frac{(H_2)^{1/2}(OH)}{(H_2O)};$$
$$K_7 = \frac{(N)^2}{(N_2)};$$
$$K_8 = \frac{(CH_4)(H_2O)}{(CO)(H_2)^3};$$
$$K_9 = \frac{(NH_3)}{(N_2)^{1/2}(H_2)^{3/2}};$$
$$K_{10} = \frac{(CO_2)}{(CO)(O_2)^{1/2}};$$

$$K_{11} = \frac{(CO)}{(O_2)^{1/2}};$$
$$K_{12} = \frac{(NO)}{(N_2)^{1/2}(O_2)^{1/2}}$$

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